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(54) Title: MULTI-LAYERED MAGNETIC PIGMENTS AND FOILS

(57) Abstract: Multilayered magnetic pigment flakes and foils are provided. The pigment flakes can be a symmetrical coating structure on opposing sides of a magnetic core, or can be formed with the encapsulating coatings around the magnetic core. The magnetic core can be a magnetic layer between reflector or dielectric layers, a dielectric layer between magnetic layers, or only a magnetic layer. Some embodiments of the pigment flakes and foils exhibit a discrete color shift so as to have distinct colors at differing angles of incident light or viewing. The pigment flakes can be interspersed into liquid media such as paints or inks to produce colorant compositions for subsequent application to objects or papers. The foils can be laminated to various objects or can be formed on a carrier substrate.

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# MULTI-LAYERED MAGNETIC PIGMENTS AND FOILS

## BACKGROUND OF THE INVENTION

### 1. The Field of the Invention

The present invention relates generally to pigments and foils. In particular, the present invention relates to multilayered pigment flakes and foils which have magnetic layers, and pigment compositions that incorporate multilayer pigment flakes having magnetic layers.

### 2. The Relevant Technology

Various pigments, colorants, and foils have been developed for a wide variety of applications. For example, magnetic pigments have been developed for use in applications such as decorative cookware, creating patterned surfaces, and security devices. Similarly, color shifting pigments have been developed for such uses as cosmetics, inks, coating materials, ornaments, ceramics, automobile paints, anti-counterfeiting hot stamps, and anti-counterfeiting inks for security documents and currency.

Color shifting pigments, colorants, and foils exhibit the property of changing color upon variation of the angle of incident light, or as the viewing angle of the observer is shifted. The color-shifting properties of pigments and foils can be controlled through proper design of the optical thin films or orientation of the molecular species used to form the flake or foil coating structure. Desired effects can be achieved through the variation of parameters such as thickness of the layers forming the flakes and foils and the index of refraction of each layer. The changes in perceived color which occur for different viewing angles or angles of incident light are a result of a combination of selective absorption of the materials comprising the layers and wavelength dependent interference effects. The interference effects, which arise from the superposition of light waves that have undergone multiple reflections, are responsible for the shifts in color perceived with different angles. The reflection maxima changes in position and intensity, as the viewing angle changes, due to changing interference effects arising from light path length differences in the various layers of a material which are selectively enhanced at particular wavelengths.

Various approaches have been used to achieve such color shifting effects. For

1 example, small multilayer flakes, typically composed of multiple layers of thin films,  
are dispersed throughout a medium such as paint or ink that may then be subsequently  
applied to the surface of an object. Such flakes may optionally be overcoated to  
achieve desired colors and optical effects. Another approach is to encapsulate small  
5 metallic or silicatic substrates with varying layers and then disperse the encapsulated  
substrates throughout a medium such as paint or ink. Additionally, foils composed of  
multiple layers of thin films on a substrate material have been made.

One manner of producing a multilayer thin film structure is by forming it on a  
flexible web material with a release layer thereon. The various layers are deposited  
10 on the web by methods well known in the art of forming thin coating structures, such  
as PVD, sputtering, or the like. The multilayer thin film structure is then removed  
from the web material as thin film color shifting flakes, which can be added to a  
polymeric medium such as various pigment vehicles for use as an ink or paint. In  
addition to the color shifting flakes, additives can be added to the inks or paints to  
15 obtain desired color shifting results.

Color shifting pigments or foils are formed from a multilayer thin film  
structure that includes the same basic layers. These include an absorber layer(s), a  
dielectric layer(s), and optionally a reflector layer, in varying layer orders. The  
coatings can be formed to have a symmetrical multilayer thin film structure, such as:

20 absorber/dielectric /reflector/dielectric/absorber ; or  
absorber/dielectric/absorber.

Coatings can also be formed to have an asymmetrical multilayer thin film structure,  
such as:

absorber/dielectric/reflector.

25 For example, U.S. Patent No. 5,135,812 to Phillips et al., which is  
incorporated by reference herein, discloses color-shifting thin film flakes having  
several different configurations of layers such as transparent dielectric and semi-  
transparent metallic layered stacks. In U.S. Patent No. 5,278,590 to Phillips et al.,  
which is incorporated by reference herein, a symmetric three layer optical interference  
30 coating is disclosed which comprises first and second partially transmitting absorber  
layers which have essentially the same material and thickness, and a dielectric spacer  
layer located between the first and second absorber layers.

Color shifting platelets for use in paints are disclosed in U.S. Patent No. 5,571,624 to Phillips et al., which is incorporated by reference herein. These platelets are formed from a symmetrical multilayer thin film structure in which a first semi-opaque layer such as chromium is formed on a substrate, with a first dielectric layer formed on the first semi-opaque layer. An opaque reflecting metal layer such as aluminum is formed on the first dielectric layer, followed by a second dielectric layer of the same material and thickness as the first dielectric layer. A second semi-opaque layer of the same material and thickness as the first semi-opaque layer is formed on the second dielectric layer.

10 With regard to magnetic pigments, U.S. Patent No. 4,838,648 to Phillips et al. (hereinafter "*Phillips '648*") discloses a thin film magnetic color shifting structure wherein the magnetic material can be used as the reflector or absorber layer. One disclosed magnetic material is a cobalt nickel alloy. *Phillips '648* discloses flakes and foils with the following structures:

15 dyed superstrate/absorber/dielectric/magnetic layer/substrate;  
dyed superstrate/absorber/dielectric/magnetic layer/dielectric/absorber/dyed  
superstrate;  
and

adhesive/magnetic layer/dielectric/absorber/releasable hardcoat/substrate.

Patterned surfaces have been provided by exposing magnetic flakes to a magnetic force to effect a physical alteration in the structure of the pigment. For example, U.S. Patent No. 6,103,361 to Batzar et al. (hereinafter "*Batzar*") uses pigments made of magnetizable materials to decorate cookware. In particular, *Batzar* is directed toward controlling the orientation of stainless steel flakes in a fluoropolymer release coating to make patterns where at least some of the flakes are longer than the coating thickness. The patterned substrate is formed by applying magnetic force through the edges of a magnetizable die positioned under a coated base to alter the orientation of the flakes within the coating, thereby inducing an imaging effect or pattern. However, *Batzar* does not discuss the use of optical thin film stacks or platelets employing a magnetic layer. In addition, although the stainless steel flakes used in *Batzar* are suitable for decorating cookware, they are poorly reflecting.

1 U.S. Patent No. 2,570,856 to Pratt et al (hereinafter "*Pratt*") is directed to metallic flake pigments which are based on ferromagnetic metal platelets. Like *Batzar*, however, *Pratt* uses poorly reflecting metals and does not teach the use of thin film optical stacks.

5 U.S. Patent Nos. 5,364,689 and 5,630,877 to Kashiwagi et al., (hereinafter collectively "the *Kashiwagi* patents"), the disclosures of which are incorporated herein by reference, disclose methods and apparatus for creating magnetically formed painted patterns. The *Kashiwagi* patents teach use of a magnetic paint layer, which includes non-spherical magnetic particles in a paint medium. A magnetic field with  
10 magnetic field lines in the shape of the desired pattern is applied to the paint layer. The final pattern is created by the different magnetic particle orientations in the hardened paint.

One attempt at incorporating a magnetic layer into a multilayer flake is disclosed in European Patent Publication EP 686675B1 to Schmid et al. (hereinafter  
15 "*Schmid*"), which describes laminar color shifting structures which include a magnetic layer between the dielectric layer and a central aluminum layer as follows:

oxide/absorber/dielectric/magnet/Al/magnet/dielectric/absorber/oxide

Thus, *Schmid* uses aluminum platelets and then coats these platelets with magnetic materials. However, the overlying magnetic material downgrades the reflective  
20 properties of the pigment because aluminum is the second brightest metal (after silver), meaning any magnetic material is less reflective. Further, *Schmid* starts with aluminum platelets generated from ballmilling, a method which is limited in terms of the layer smoothness that can be achieved.

Patent Publication EP 710508A1 to Richter et al. (hereinafter "*Richter*")  
25 discloses methods for providing three dimensional effects by drawing with magnetic tips. *Richter* describes three dimensional effects achieved by aligning magnetically active pigments in a spatially-varying magnetic field. *Richter* uses standard pigments (barium ferrite, strontium ferrite, samarium/cobalt, Al/Co/Ni alloys, and metal oxides made by sintering and quick quenching, none of which are composed of optical thin  
30 film stacks. Rather, the particles are of the hard magnetic type. *Richter* uses electromagnetic pole pieces either on top of the coating or on both sides of the coating. However, *Richter* uses a moving system and requires "drawing" of the

1 image. This "drawing" takes time and is not conducive to production type processes.

U.S. Patent No. 3,791,864 to Steingroever (hereinafter "*Steingroever*") describes a method for patterning magnetic particles by orienting them with a magnetic pattern generated in an underlying prime coating that has previously been  
5 patterned by a magnetic field. The prime coat contains magnetic particles of the type  $MO \times 6Fe_2O_3$  where M can be one or more of the elements Ba, Sr, Co, or Pb. After coating a continuous sheet of liquid coating of the primer, it is hardened and then areas of the primer are magnetized by a magnetic field. Next, a pigment vehicle with magnetic particles suspended therein is then applied. The magnetic particles  
10 suspended therein are finally oriented by the magnetic force from the magnetic pattern in the primer, creating the final pattern. However, *Steingroever* suffers from a diffuse magnetic image in the prime coat, which in turn passes a diffuse image to the topcoat. This reduction in resolution is because high magnetic fields are limited in the resolution they can create. This limitation is due to high magnetic field lines  
15 surrounding the intended magnetic image, thereby affecting untargeted magnetic particles in the prime coat and blurring the image.

Accordingly, there is a need for improved multilayer pigment flakes and foils with magnetic properties that overcome or avoid the above problems and limitations.

20

#### **SUMMARY OF THE INVENTION**

In accordance with the invention as embodied and broadly described herein, pigment flakes and foils are provided which have magnetic properties. The pigment flakes can have a symmetrical stacked coating structure on opposing sides of a magnetic core layer, can have an asymmetrical coating structure with all of the layers  
25 on one side of the magnetic layer, or can be formed with one or more encapsulating coatings around a magnetic core. The coating structure of the flakes and foils includes at least one magnetic layer and optionally one or more of a reflector layer, dielectric layer, and absorber layer. In color shifting embodiments of the invention, the coating structure includes the dielectric layer overlying the magnetic and reflector  
30 layers, and the absorber layer overlying the dielectric layer. Non color shifting embodiments of the invention include a magnetic layer between two reflector layers or encapsulated by a reflector layer, a magnetic layer between two dielectric layers or

1 encapsulated by a dielectric layer, a dielectric layer between two magnetic layers or  
encapsulated by a magnetic layer, and a magnetic layer encapsulated by a colorant  
layer.

5 The color shifting embodiments exhibit a discrete color shift so as to have a  
first color at a first angle of incident light or viewing and a second color different  
from the first color at a second angle of incident light or viewing. The pigment flakes  
can be interspersed into liquid media such as paints or inks to produce colorant  
compositions for subsequent application to objects or papers. The foils can be  
laminated to various objects or can be formed on a carrier substrate.

10 These and other features of the present invention will become more fully  
apparent from the following description and appended claims, or may be learned by  
the practice of the invention as set forth hereinafter.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

15 In order to illustrate the manner in which the above-recited and other  
advantages and features of the invention are obtained, a more particular description of  
the invention briefly described above will be rendered by reference to specific  
embodiments thereof which are illustrated in the appended drawings. Understanding  
that these drawings depict only typical embodiments of the invention and are not  
20 therefore to be considered limiting of its scope, the invention will be described and  
explained with additional specificity and detail through the use of the accompanying  
drawings in which:

Figure 1 is a schematic representation of the coating structure of a magnetic  
flake according to one embodiment of the invention;

25 Figure 2 is a schematic representation of the coating structure of a magnetic  
flake according to another embodiment of the invention;

Figure 3 is a schematic representation of the coating structure of a magnetic  
flake according to an alternative embodiment of the invention;

30 Figure 4 is a schematic representation of the coating structure of a magnetic  
flake according to another embodiment of the invention;

Figure 5 is a schematic representation of the coating structure of a magnetic  
flake according to a further embodiment of the invention;

1        Figure 6 is a schematic representation of the coating structure of a magnetic flake according to a further embodiment of the invention;

      Figure 7 is a schematic representation of the coating structure of a magnetic flake according to an alternative embodiment of the invention;

5        Figure 8 is a schematic representation of the coating structure of a magnetic flake according to a further embodiment of the invention;

      Figure 9 is a schematic representation of the coating structure of a magnetic flake according to yet a further embodiment of the invention;

10       Figure 10 is a schematic representation of the coating structure of a magnetic flake according to another alternative embodiment of the invention;

      Figure 11 is a schematic representation of the coating structure of a magnetic flake according to another embodiment of the invention;

      Figure 12 is a schematic representation of the coating structure of a magnetic flake according to a further embodiment of the invention;

15       Figure 13 is a schematic representation of the coating structure of a magnetic foil according to one embodiment of the invention;

      Figure 14 is a schematic representation of the coating structure of a magnetic foil according to another embodiment of the invention;

20       Figure 15 is a schematic representation of the coating structure of a magnetic foil according to a further embodiment of the invention;

      Figure 16 is a schematic representation of the coating structure of an optical article according to an additional embodiment of the invention; and

      Figure 17 is a schematic representation of the coating structure of an optical article according to a further embodiment of the invention.

25

### **DETAILED DESCRIPTION OF THE INVENTION**

      The present invention relates to multilayer pigment flakes and foils which have magnetic layers, and pigment compositions which incorporate the magnetic flakes. The flakes and foils can be used both to create security features which are not  
30       visually perceptible, and to create three dimensional-like images for security devices or to add decorative features to a product. The nonvisual security features are provided by burying the magnetic layer between other layers within a flake or foil so

1 that only the overlying layers are exposed.

The three dimensional-like effects can be provided by exposing the flake or foil to an external magnetic force, thereby orienting the plane of some of the pigments normal to the surface of the coating. The un-oriented pigments lie with their planar surface parallel to the surface of the coating. The three dimensional-like effect is due to the alignment of the particles such that the aspect ratio is oriented with the magnetic field, *i.e.* the longest part of the pigment aligns itself along the magnetic field lines. In such case, the face of the pigment is turned away from the observer to various extents depending on the magnitude of the magnetic force. In the limit or maximum orientation, the coating appears black in color. As one moves off the black, one moves slowly toward the color of the planar surface of the pigment, *i.e.*, color shifting, non-color shifting, such as the color blue, or silver as for example, aluminum. The result is a colored three dimensional-like effect, similar to that of a holographic effect, that appears to move as the viewing angle changes. Methods of creating three dimensional-like images using the magnetic pigments disclosed herein are described in further detail in a copending U.S. Patent Application, bearing attorney docket No. 13676.167, and entitled Methods For Producing Imaged Coated Articles By Using Magnetic Pigments, the disclosure of which is incorporated herein by reference.

20 Unlike many prior magnetic flakes, the presently disclosed flakes are not composed only of magnetizable materials, but include both magnetizable and non-magnetizable materials. For example, the invention encompasses pigment flakes wherein a magnetic layer is buried within one or more reflector layers. In another embodiment the pigment flakes comprise a magnetic core surrounded by dielectric layers. In yet a further embodiment, the pigment flakes include a dielectric core surrounded by magnetic layers.

In the case of magnetic layers buried between or within overlying reflector layers, the present invention presents a significant improvement over the prior art by substantially achieving higher chroma and brightness. By putting the duller magnetic material inside the reflector, the present invention accomplishes two objectives: 1) the reflectivity of the reflector layer is maintained; and 2) color shifting pigments without the inner core of magnetic material cannot be distinguished by an observer from such

1 pigment with the core of magnetic material. For example, two coated objects viewed  
side by side, one with and one without the magnetic material in the coating, would  
look the same to the observer. However, the magnetic color shifting pigment  
provides a covert security feature in addition to the color shifting effect. Thus, with a  
5 magnetic detection system, a magnetic covert signature in the pigment could be read  
by a Faraday rotator detector, for example.

In various embodiments of the present invention, the pigment flakes and foils  
have substantial shifts in chroma and hue with changes in angle of incident light or  
viewing angle of an observer. Such an optical effect, known as goniochromaticity or  
10 "color shift," allows a perceived color to vary with the angle of illumination or  
observation. Accordingly, such pigment flakes and foils exhibit a first color at a first  
angle of incident light or viewing and a second color different from the first color at a  
second angle of incident light or viewing. The pigment flakes can be interspersed into  
liquid media such as paints or inks to produce various color shifting colorant  
15 compositions for subsequent application to objects or papers. The foils can be  
laminated to various objects or can be formed on a carrier substrate.

Generally, the color shifting pigment flakes can have a symmetrical stacked  
coating structure on opposing sides of a magnetic core layer, can have an  
asymmetrical coating structure with a majority of the layers on one side of the  
20 magnetic layer, or can be formed with one or more encapsulating coatings which  
surround a magnetic core. The coating structure of the flakes and foils generally  
includes a magnetic core, which includes a magnetic layer and other optional layers, a  
dielectric layer overlying the magnetic core, and an absorber layer overlying the  
dielectric layer.

25 The color shifting flakes and foils of the invention can be formed using  
conventional thin film deposition techniques, which are well known in the art of  
forming thin coating structures. Nonlimiting examples of such thin film deposition  
techniques include physical vapor deposition (PVD), chemical vapor deposition  
(CVD), plasma enhanced (PE) variations thereof such as PECVD or downstream  
30 PECVD, sputtering, electrolysis deposition, and other like deposition methods that  
lead to the formation of discrete and uniform thin film layers.

The color shifting pigment flakes of the invention can be formed by various

1 fabrication methods. For example, the pigment flakes can be formed by a web  
coating process in which various layers are sequentially deposited on a web material  
by conventional deposition techniques to form a thin film structure, which is  
subsequently fractured and removed from the web, such as by use of a solvent, to  
5 form a plurality of thin film flakes.

In another fabrication method, one or more thin film layers including at least  
the magnetic layer is deposited on a web to form a film, which is subsequently  
fractured and removed from the web to form a plurality of pigment preflakes. The  
preflakes can be fragmented further by grinding if desired. The preflakes are then  
10 coated with the remaining layer or layers in a sequential encapsulation process to  
form a plurality of pigment flakes. A similar process is disclosed in further detail in  
copending U.S. Application Serial No. 09/512,116, filed on February 24, 2000, the  
disclosure of which is incorporated by reference herein.

In another fabrication method, magnetic particles can be coated in a sequential  
15 encapsulation process to form a plurality of pigment flakes. When an encapsulation  
process is used for forming the outer layers of the flakes, it will be appreciated that  
each respective encapsulating layer is a continuous layer composed of one material  
and having substantially the same thickness around the flake structure. In some  
embodiments of the invention, the encapsulating layer can be a colored dielectric  
20 material or an organic layer with added colorant.

Referring now to the drawings, wherein like structures are provided with like  
reference designations, the drawings only show the structures necessary to understand  
the present invention. Figure 1 depicts a reflective magnetic flake ("RMF") 20  
according to one embodiment of the invention. The RMF 20 is a three layer design  
25 having a generally symmetrical thin film structure with a central magnetic layer 22  
and at least one reflector layer on either or both of the opposing major surfaces of the  
central magnetic layer. Thus, RMF 20 comprises a magnetic layer interdisposed  
between a reflector layer 24 and an opposing reflector layer 26. By inserting the  
magnetic layer between the highly reflective reflector layers, such as aluminum, the  
30 optical properties of the reflector layers are not degraded and the flake remains highly  
reflective. The RMF 20 can be used as a pigment flake or can be used as a core  
section with additional layers applied thereover such as in a color shifting pigment. In

1 the case of color shifting pigments, maintaining the high reflective layer is extremely important to preserve high brightness and chroma. Each of these layers in the coating structure of RMF 20 is discussed below in greater detail.

5 The magnetic layer 22 can be formed of any magnetic material such as nickel, cobalt, iron, gadolinium, terbium, dysprosium, erbium, and their alloys or oxides. For example, a cobalt nickel alloy can be employed, with the cobalt and nickel having a ratio by weight of about 80% and about 20%, respectively. This ratio for each of these metals in the cobalt nickel alloy can be varied by plus or minus about 10% and still achieve the desired results. Thus, cobalt can be present in the alloy in an amount  
10 from about 70% to about 90% by weight, and nickel can be present in the alloy in an amount from about 10% to about 30% by weight. Other examples of alloys include Fe/Si, Fe/Ni, FeCo, Fe/Ni/Mo, and combinations thereof. Hard magnetics of the type SmCo<sub>5</sub>, NdCo<sub>5</sub>, Sm<sub>2</sub>Co<sub>17</sub>, Nd<sub>2</sub>Fe<sub>14</sub>B, Sr<sub>6</sub>Fe<sub>2</sub>O<sub>3</sub>, TbFe<sub>2</sub>, Al-Ni-Co, and combinations thereof, can also be used as well as spinel ferrites of the type Fe<sub>3</sub>O<sub>4</sub>, NiFe<sub>2</sub>O<sub>4</sub>,  
15 MnFe<sub>2</sub>O<sub>4</sub>, CoFe<sub>2</sub>O<sub>4</sub>, or garnets of the type YIG or GdIG, and combinations thereof. The magnetic material may be selected for its reflecting or absorbing properties as well as its magnetic properties. When utilized to function as a reflector, the magnetic material is deposited to a thickness so that it is substantially opaque. When utilized as an absorber, the magnetic material is deposited to a thickness so that it is not  
20 substantially opaque. A typical thickness for the magnetic material when utilized as an absorber is from about 2 nm to about 20 nm.

Although this broad range of magnetic materials can be used, the "soft" magnets are preferred in some embodiments of the invention. As used herein, the term "soft magnets" refers to any material exhibiting ferromagnetic properties but  
25 having a remanence that is substantially zero after exposure to a magnetic force. Soft magnets show a quick response to an applied magnetic field, but have very low (coercive fields ( $H_c$ ) = 0.05-300 Oersteds (Oe)) or zero magnetic signatures, or retain very low magnetic lines of force after the magnetic field is removed. Similarly, as used herein, the term "hard magnets" (also called permanent magnets) refers to any  
30 material that exhibits ferromagnetic properties and that has a long lasting remanence after exposure to a magnetizing force. A ferromagnetic material is any material that has a permeability substantially greater than 1 and that exhibits magnetic hysteresis

1 properties.

Preferably, the magnetic materials used to form magnetic layers in the flakes and foils of the invention have a coercivity of less than about 2000 Oe, more preferably less than about 300 Oe. Coercivity refers to the ability of a material to be  
5 demagnetized by an external magnetic field. The higher the value of coercivity, the higher the magnetic field required to de-magnetize the material after the field is removed. In some embodiments of the invention, the magnetic layers used are preferably "soft" magnetic materials (easily demagnetized), as opposed to "hard" magnetic materials (difficult to demagnetize) which have higher coercivities. The  
10 coercivities of the foils, pigments or colorants of the magnetic color shifting designs according to the invention are preferably in a range of about 50 Oe to about 300 Oe. These coercivities are lower than in standard recording materials. Thus, preferred embodiments of the invention which use soft magnets in magnetic color shifting pigments and magnetic non color shifting pigments are an improvement over  
15 conventional technologies. The use of soft magnetic materials in pigment flakes allows for easier dispersion of the flakes without clumping.

The magnetic layer 22 can be formed to have a suitable physical thickness of from about 200 angstroms (Å) to about 10,000 Å, and preferably from about 500 Å to about 1,500 Å. However, it will be appreciated by those skilled in the art, in view of  
20 the disclosure herein, that the optimal magnetic thickness will vary depending on the particular magnetic material used and the purpose for its use. For example, a magnetic absorber layer will be thinner than a magnetic reflector layer based on the optical requirements for such layers, while a covert magnetic layer will have a thickness based solely on its magnetic properties.

25 The reflector layers 24 and 26 can be composed of various reflective materials. Presently preferred materials are one or more metals, one or more metal alloys, or combinations thereof, because of their high reflectivity and ease of use, although non-metallic reflective materials could also be used. Nonlimiting examples of suitable metallic materials for the reflector layers include aluminum, silver, copper,  
30 gold, platinum, tin, titanium, palladium, nickel, cobalt, rhodium, niobium, chromium, and combinations or alloys thereof. These can be selected based on the f desired. The reflector layers 24, 26 can be formed to have a suitable physical thickness of from

1 about 400 Å to about 2,000 Å, and preferably from about 500 Å to about 1,000 Å.

In an alternative embodiment, opposing dielectric layers may optionally be added to overlie reflector layers 24 and 26. These opposing dielectric layers add durability, rigidity, and corrosion resistance to RMF 20. Alternatively, an  
5 encapsulating dielectric layer may be formed to substantially surround reflector layers 24, 26 and magnetic layer 22. The dielectric layer(s) may be optionally clear, or may be selectively absorbing so as to contribute to the color effect of the pigment flake. Examples of suitable dielectric materials for the dielectric layers are described hereafter.

10 Figure 2 depicts a magnetic color shifting pigment flake 40 based upon a RMF according to one embodiment of the invention. The flake 40 is a generally symmetrical multilayer thin film structure having layers on opposing sides of a RMF 42. Thus, first and second dielectric layers 44 and 46 are disposed respectively on  
15 opposing sides of RMF 42, and first and second absorber layers 48 and 50 are disposed respectively on each of dielectric layers 44 and 46. The RMF is as discussed hereinabove for Figure 1 while the dielectric and absorber layers are discussed below in greater detail.

The dielectric layers 44 and 46 act as spacers in the thin film stack structure of flake 40. These layers are formed to have an effective optical thickness for imparting  
20 interference color and desired color shifting properties. The dielectric layers may be optionally clear, or may be selectively absorbing so as to contribute to the color effect of a pigment. The optical thickness is a well known optical parameter defined as the product  $\eta d$ , where  $\eta$  is the refractive index of the layer and  $d$  is the physical thickness of the layer. Typically, the optical thickness of a layer is expressed in terms of a  
25 quarter wave optical thickness (QWOT) that is equal to  $4\eta d/\lambda$ , where  $\lambda$  is the wavelength at which a QWOT condition occurs. The optical thickness of dielectric layers can range from about 2 QWOT at a design wavelength of about 400 nm to about 9 QWOT at a design wavelength of about 700 nm, and preferably 2-6 QWOT at  
30 400-700 nm, depending upon the color shift desired. The dielectric layers typically have a physical thickness of about 100 nm to about 800 nm, depending on the color characteristics desired.

Suitable materials for dielectric layers 44 and 46 include those having a "high"

1 index of refraction, defined herein as greater than about 1.65, as well as those have a  
"low" index of refraction, which is defined herein as about 1.65 or less. Each of the  
dielectric layers can be formed of a single material or with a variety of material  
combinations and configurations. For example, the dielectric layers can be formed of  
5 only a low index material or only a high index material, a mixture or multiple  
sublayers of two or more low index materials, a mixture or multiple sublayers of two  
or more high index materials, or a mixture or multiple sublayers of low index and  
high index materials. In addition, the dielectric layers can be formed partially or  
entirely of high/low dielectric optical stacks, which are discussed in further detail  
10 below. When a dielectric layer is formed partially with a dielectric optical stack, the  
remaining portion of the dielectric layer can be formed with a single material or  
various material combinations and configurations as described above.

Examples of suitable high refractive index materials for the dielectric layer  
include zinc sulfide (ZnS), zinc oxide (ZnO), zirconium oxide ( $ZrO_2$ ), titanium  
15 dioxide ( $TiO_2$ ), diamond-like carbon, indium oxide ( $In_2O_3$ ), indium-tin-oxide (ITO),  
tantalum pentoxide ( $Ta_2O_5$ ), ceric oxide ( $CeO_2$ ), yttrium oxide ( $Y_2O_3$ ), europium  
oxide ( $Eu_2O_3$ ), iron oxides such as (II)diiron(III) oxide ( $Fe_3O_4$ ) and ferric oxide  
( $Fe_2O_3$ ), hafnium nitride (HfN), hafnium carbide (HfC), hafnium oxide ( $HfO_2$ ),  
lanthanum oxide ( $La_2O_3$ ), magnesium oxide (MgO), neodymium oxide ( $Nd_2O_3$ ),  
20 praseodymium oxide ( $Pr_6O_{11}$ ), samarium oxide ( $Sm_2O_3$ ), antimony trioxide ( $Sb_2O_3$ ),  
silicon monoxide (SiO), selenium trioxide ( $Se_2O_3$ ), tin oxide ( $SnO_2$ ), tungsten trioxide  
( $WO_3$ ), combinations thereof, and the like.

Suitable low refractive index materials for the dielectric layer include silicon  
dioxide ( $SiO_2$ ), aluminum oxide ( $Al_2O_3$ ), metal fluorides such as magnesium fluoride  
25 ( $MgF_2$ ), aluminum fluoride ( $AlF_3$ ), cerium fluoride ( $CeF_3$ ), lanthanum fluoride ( $LaF_3$ ),  
sodium aluminum fluorides (e.g.,  $Na_3AlF_6$  or  $Na_5Al_3F_{14}$ ), neodymium fluoride  
( $NdF_3$ ), samarium fluoride ( $SmF_3$ ), barium fluoride ( $BaF_2$ ), calcium fluoride ( $CaF_2$ ),  
lithium fluoride (LiF), combinations thereof, or any other low index material having  
an index of refraction of about 1.65 or less. For example, organic monomers and  
30 polymers can be utilized as low index materials, including dienes or alkenes such as  
acrylates (e.g., methacrylate), perfluoroalkenes, polytetrafluoroethylene (Teflon),  
fluorinated ethylene propylene (FEP), combinations thereof, and the like.

1       It should be appreciated that several of the above-listed dielectric materials are  
typically present in non-stoichiometric forms, often depending upon the specific  
method used to deposit the dielectric material as a coating layer, and that the above-  
listed compound names indicate the approximate stoichiometry. For example, silicon  
5       monoxide and silicon dioxide have nominal 1:1 and 1:2 silicon:oxygen ratios,  
respectively, but the actual silicon:oxygen ratio of a particular dielectric coating layer  
varies somewhat from these nominal values. Such non-stoichiometric dielectric  
materials are also within the scope of the present invention.

As mentioned above, the dielectric layers can be formed of high/low dielectric  
10       optical stacks, which have alternating layers of low index (L) and high index (H)  
materials. When a dielectric layer is formed of a high/low dielectric stack, the color  
shift at angle will depend on the combined refractive index of the layers in the stack.  
Examples of suitable stack configurations for the dielectric layers include LH, HL,  
LHL, HLH, HLHL, LHLH, or in general (LHL)<sup>n</sup> or (HLH)<sup>n</sup>, where n = 1-100, as well  
15       as various multiples and combinations thereof. In these stacks, LH, for example,  
indicates discrete layers of a low index material and a high index material. In an  
alternative embodiment, the high/low dielectric stacks are formed with a gradient  
index of refraction. For example, the stack can be formed with layers having a graded  
index low-to-high, a graded index high-to-low, a graded index [low-to-high-to-low]<sup>n</sup>,  
20       a graded index [high-to-low-to-high]<sup>n</sup>, where n = 1-100, as well as combinations and  
multiples thereof. The graded index is produced by a gradual variance in the  
refractive index, such as low-to-high index or high-to-low index, of adjacent layers.  
The graded index of the layers can be produced by changing gases during deposition  
or co-depositing two materials (*e.g.*, L and H) in differing proportions. Various  
25       high/low optical stacks can be used to enhance color shifting performance, provide  
antireflective properties to the dielectric layer, and change the possible color space of  
the pigments of the invention.

The dielectric layers can each be composed of the same material or a different  
material, and can have the same or different optical or physical thickness for each  
30       layer. It will be appreciated that when the dielectric layers are composed of different  
materials or have different thicknesses, the flakes exhibit different colors on each side  
thereof and the resulting mix of flakes in a pigment or paint mixture would show a

1 new color which is the combination of the two colors. The resulting color would be  
based on additive color theory of the two colors coming from the two sides of the  
flakes. In a multiplicity of flakes, the resulting color would be the additive sum of the  
two colors resulting from the random distribution of flakes having different sides  
5 oriented toward the observer.

The absorber layers 48, 50 of flake 40 can be composed of any absorber  
material having the desired absorption properties, including materials that are  
uniformly absorbing or non-uniformly absorbing in the visible part of the  
electromagnetic spectrum. Thus, selective absorbing materials or nonselective  
10 absorbing materials can be used, depending on the color characteristics desired. For  
example, the absorber layers can be formed of nonselective absorbing metallic  
materials deposited to a thickness at which the absorber layer is at least partially  
absorbing, or semi-opaque. Nonlimiting examples of suitable absorber materials  
include metallic absorbers such as chromium, aluminum, nickel, silver, copper,  
15 palladium, platinum, titanium, vanadium, cobalt, iron, tin, tungsten, molybdenum,  
rhodium, and niobium, as well as their corresponding oxides, sulfides, and carbides.  
Other suitable absorber materials include carbon, graphite, silicon, germanium,  
cermet, ferric oxide or other metal oxides, metals mixed in a dielectric matrix, and  
other substances that are capable of acting as a uniform or selective absorber in the  
20 visible spectrum. Various combinations, mixtures, compounds, or alloys of the above  
absorber materials may be used to form the absorber layers of flake 40.

Examples of suitable alloys of the above absorber materials include Inconel  
(Ni-Cr-Fe), stainless steels, Hastalloys (e.g., Ni-Mo-Fe; Ni-Mo-Fe-Cr; Ni-Si-Cu) and  
titanium-based alloys, such as titanium mixed with carbon (Ti/C), titanium mixed  
25 with tungsten (Ti/W), titanium mixed with niobium (Ti/Nb), and titanium mixed with  
silicon (Ti/Si), and combinations thereof. As mentioned above, the absorber layers  
can also be composed of an absorbing metal oxide, metal sulfide, metal carbide, or  
combinations thereof. For example, one preferred absorbing sulfide material is silver  
sulfide. Other examples of suitable compounds for the absorber layers include  
30 titanium-based compounds such as titanium nitride (TiN), titanium oxynitride  
( $\text{TiN}_x\text{O}_y$ ), titanium carbide (TiC), titanium nitride carbide ( $\text{TiN}_x\text{C}_z$ ), titanium  
oxynitride carbide ( $\text{TiN}_x\text{O}_y\text{C}_z$ ), titanium silicide ( $\text{TiSi}_2$ ), titanium boride ( $\text{TiB}_2$ ), and

1 combinations thereof. In the case of  $\text{TiN}_x\text{O}_y$  and  $\text{TiN}_x\text{O}_y\text{C}_z$ , preferably  $x = 0$  to  $1$ ,  $y = 0$  to  $1$ , and  $z = 0$  to  $1$ , where  $x + y = 1$  in  $\text{TiN}_x\text{O}_y$  and  $x + y + z = 1$  in  $\text{TiN}_x\text{O}_y\text{C}_z$ . For  $\text{TiN}_xC_z$ , preferably  $x = 0$  to  $1$  and  $z = 0$  to  $1$ , where  $x + z = 1$ . Alternatively, the absorber layers can be composed of a titanium-based alloy disposed in a matrix of Ti,  
5 or can be composed of Ti disposed in a matrix of a titanium-based alloy.

It will be appreciated by one skilled in the art that the absorber layer also could be formed of a magnetic material, such as a cobalt nickel alloy. This simplifies the manufacture of the magnetic color shifting device or structure by reducing the number of materials required.

10 The absorber layers are formed to have a physical thickness in the range from about  $30 \text{ \AA}$  to about  $500 \text{ \AA}$ , and preferably about  $50 \text{ \AA}$  to about  $150 \text{ \AA}$ , depending upon the optical constants of the absorber layer material and the desired peak shift. The absorber layers can each be composed of the same material or a different material, and can have the same or different physical thickness for each layer.

15 In an alternative embodiment of flake 40, an asymmetrical color shifting flake can be provided which includes a thin film stack structure with the same layers as on one side of RMF 42 as shown in Figure 2. Accordingly, the asymmetrical color shifting flake includes RMF 42, dielectric layer 44 overlying RMF 42, and absorber layer 48 overlying dielectric layer 44. Each of these layers can be composed of the  
20 same materials and have the same thicknesses as described above for the corresponding layers of flake 40. In addition, asymmetrical color shifting flakes can be formed by a web coating process such as described above in which the various layers are sequentially deposited on a web material to form a thin film structure, which is subsequently fractured and removed from the web to form a plurality of  
25 flakes.

In a further alternative embodiment, flake 40 can be formed without the absorber layers. In this embodiment, opposing dielectric layers 44 and 46 are formed of high/low (H/L) dielectric optical stacks such as described previously. Thus, dielectric layers 44 and 46 can be configured such that flake 40 has the coating  
30 structures:  $(\text{HL})^n/\text{RMF}/(\text{LH})^n$ ,  $(\text{LH})^n/\text{RMF}/(\text{HL})^n$ ,  $(\text{LHL})^n/\text{RMF}/(\text{LHL})^n$ ,  $(\text{HLH})^n/\text{RMF}/(\text{HLH})^n$ , or other similar configurations, where  $n = 1-100$  and the L and H layers are 1 quarterwave (QW) at a design wavelength.

1        Figure 3 depicts a reflective magnetic flake or particle ("RMP") 60 according  
to another embodiment of the invention. The RMP 60 is a two layer design with a  
reflector layer 62 substantially surrounding and encapsulating a core magnetic layer  
64. By inserting the magnetic layer within the reflector layer, the optical properties of  
5        the reflector layer are not downgraded and the reflector layer remains highly  
reflective. The RMP 60 can be used as a pigment particle or can be used as a core  
section with additional layers applied thereover. The magnetic layer and reflector  
layer can be composed of the same materials discussed with respect to RMF 20.

10        In an alternative embodiment, a dielectric layer may optionally be added to  
overlie reflector layer 62, to add durability, rigidity, and corrosion resistance to RMP  
60. The dielectric layer may be optionally clear, or may be selectively absorbing so  
as to contribute to the color effect of the pigment flake.

15        Figure 4 depicts alternative coating structures (with phantom lines) for a  
magnetic color shifting pigment flake 80 in the form of an encapsulate based upon  
either the RMF or the RMP according to other embodiments of the invention. The  
flake 80 has a magnetic core section 82, which is either a RMF or a RMP, which can  
be overcoated by an encapsulating dielectric layer 84 substantially surrounding  
magnetic core section 82. An absorber layer 86, which overcoats dielectric layer 84,  
provides an outer encapsulation of flake 80. The hemispherical dashed lines on one  
20        side of flake 80 in Figure 4 indicate that dielectric layer 84 and absorber layer 86 can  
be formed as contiguous layers around magnetic core section 82.

25        Alternatively, the magnetic core section 82 and dielectric layer can be in the  
form of a thin film core flake stack, in which opposing dielectric layers 84a and 84b  
are preformed on the top and bottom surfaces but not on at least one side surface of  
magnetic core section 82 (RMF), with absorber layer 86 encapsulating the thin film  
stack. An encapsulation process can also be used to form additional layers on flake  
80 such as a capping layer (not shown). The pigment flake 80 exhibits a discrete  
color shift such that the pigment flake has a first color at a first angle of incident light  
or viewing and a second color different from the first color at a second angle of  
30        incident light or viewing.

      In a further alternative embodiment, flake 80 can be formed without the  
absorber layer. In this embodiment, dielectric layer 84 is formed of contiguous

1 high/low (H/L) dielectric optical coatings similar to the dielectric optical stacks described previously. Thus, dielectric layer 84 can have the coating structure (HL)<sup>n</sup>, (LH)<sup>n</sup>, (LHL)<sup>n</sup>, (HLH)<sup>n</sup>, or other similar configurations, where n = 1-100 and the L and H layers are 1 QW at a design wavelength.

5 Figure 5 depicts another alternative coating structure for a color shifting pigment flake 100 according to the present invention. The flake 100 includes a magnetic core section 82 and a single dielectric layer 84, which extends over top and bottom surfaces of magnetic core section 82 to form a dielectric-coated preflake 86. The core section 82 can be an RMF, RMP, or a magnetic layer. The dielectric-coated  
10 preflake 86 has two side surfaces 88 and 90. Although side surface 90 is homogeneous and formed only of the dielectric material of dielectric layer 84, side surface 88 has distinct surface regions 88a, 88b, 88c of dielectric, magnetic core section, and dielectric, respectively. The dielectric-coated preflake 86 is further coated on all sides with an absorber layer 92. The absorber layer 92 is in contact with  
15 dielectric layer 84 and magnetic core section 82 at side surface 88.

The structure of pigment flake 100 typically occurs because of a preflake coating process similar to the one disclosed in U.S. Application Serial No. 09/512,116 described previously. The preflakes can be a dielectric-coated flake, in which a dielectric coating completely encapsulates an RMF or RMP (see Figure 4), or a  
20 magnetic layer (see Figure 10). The preflakes are broken into sized preflakes using any conventional fragmentation process, such as by grinding. The sized preflakes will include some sized preflakes having top and bottom dielectric layers with no dielectric coating on the side surfaces of the preflake, such as shown for the embodiment of flake 40 in Figure 2 in which RMF 42 is coated with top and bottom  
25 dielectric layers 44 and 46. Other sized preflakes will have a single dielectric layer extending over both top and bottom surfaces of the magnetic core flake section, leaving one side surface of the magnetic core flake section exposed, such as shown for dielectric-coated preflake 86 in Figure 5. Because of the fragmentation process, substantially all of the sized preflakes have at least a portion of a side surface  
30 exposed. The sized preflakes are then coated on all sides with an absorber layer, such as shown in the flakes of Figures 4 and 5.

1        Figure 6 depicts a composite magnetic flake ("CMF") 120 which comprises a  
central dielectric support layer 122 with first and second magnetic layers 124, 126 on  
opposing major surfaces thereof. By inserting the dielectric layer between the  
magnetic layers, the CMF 120 is significantly stabilized and strengthened, having  
5        increased rigidity. Additional dielectric layers (not shown) may optionally be added  
to overlie magnetic layers 124, 126. These additional dielectric layers add durability,  
rigidity, and corrosion resistance to CMF 120. The CMF 120 can be used as a  
pigment flake by itself or can be used as a magnetic core section with additional  
layers applied thereover. The magnetic layers 124, 126 can be formed of any of the  
10        magnetic materials described previously.

The dielectric material used for support layer 122 is preferably inorganic, since  
inorganic dielectric materials have been found to have good characteristics of  
brittleness and rigidity. Various dielectric materials that can be utilized include metal  
fluorides, metal oxides, metal sulfides, metal nitrides, metal carbides, combinations  
15        thereof, and the like. The dielectric materials may be in either a crystalline,  
amorphous, or semicrystalline state. These materials are readily available and easily  
applied by physical or chemical vapor deposition processes. Examples of suitable  
dielectric materials include magnesium fluoride, silicon monoxide, silicon dioxide,  
aluminum oxide, titanium dioxide, tungsten oxide, aluminum nitride, boron nitride,  
20        boron carbide, tungsten carbide, titanium carbide, titanium nitride, silicon nitride, zinc  
sulfide, glass flakes, diamond-like carbon, combinations thereof, and the like.  
Alternatively, support layer 122 may be composed of a preformed dielectric or  
ceramic preflake material having a high aspect ratio such as a natural platelet mineral  
(*e.g.*, mica peroskovite or talc), or synthetic platelets formed from glass, alumina,  
25        silicon dioxide, carbon, micaeous iron oxide, coated mica, boron nitride, boron  
carbide, graphite, bismuth oxychloride, various combinations thereof, and the like.

In an alternative embodiment, instead of a dielectric support layer 122, various  
semiconductive and conductive materials having a sufficient ratio of tensile to  
compressive strength can function as a support layer. Examples of such materials  
30        include silicon, metal silicides, semiconductive compounds formed from any of the  
group III, IV, or V elements, metals having a body centered cubic crystal structure,  
cermet compositions or compounds, semiconductive glasses, various combinations

1 thereof, and the like. It will be appreciated from the teachings herein, however, that  
any support material providing the functionality described herein and capable of  
acting as a rigid layer with glass-like qualities would be an acceptable substitute for  
one of these materials.

5 The thickness of support layer 122 can be in a range from about 10 nm to  
about 1,000 nm, preferably from about 50 nm to about 200 nm, although these ranges  
should not be taken as restrictive.

Figure 7 depicts a composite magnetic particle ("CMP") 140 according to  
another embodiment of the invention. The CMP 140 is a two layer design with a  
10 magnetic layer 142 substantially surrounding and encapsulating a central support  
layer 144 such as a dielectric layer. By inserting the support layer within the  
magnetic layer, CMP 140 is significantly stabilized and rigid. The support layer adds  
rigidity and durability to the pigment flake. The magnetic layer 142 can be formed of  
any of the magnetic materials described previously. The support layer 144 can be  
15 formed of the same materials described hereinabove for support layer 122 of CMF  
120. The CMP 140 can be used as a pigment particle by itself or can be used as a  
magnetic core section with additional layers applied thereover. For example, an outer  
dielectric layer may be added to overlie and encapsulate magnetic layer 142. This  
outer dielectric layer adds durability, rigidity, and corrosion resistance to CMP 140.

20 Figure 8 depicts a coating structure for a color shifting pigment flake 160 in  
the form of an encapsulate. The flake 160 has a thin core layer 162, which can be  
formed of a dielectric or other material as taught hereinabove for support layer 122.  
The core layer 162 is overcoated on all sides with a magnetic layer 164, which can be  
composed of the same materials as described above for magnetic layer 22 of RMF 20.  
25 Optionally, a reflector layer 168 can be applied over magnetic layer 164. Suitable  
materials for reflector layer 168 include those materials described for reflector layer  
24 of RMF 20. The reflector layer effectively provides the reflective function of flake  
160, shielding magnetic layer 164 from being optically present. The core layer 162  
and magnetic layer 164 can be provided as a CMP 166 which is overcoated with the  
30 other layers. Alternatively CMP 166 can be replaced with a CMF such as shown in  
Figure 6. An encapsulating dielectric layer 170 substantially surrounds reflector layer  
168 and magnetic layer 164. An absorber layer 172, which overlays dielectric layer

1 170, provides an outer encapsulation of flake 160.

Various coating processes can be utilized in forming the dielectric and absorber coating layers by encapsulation. For example, suitable preferred methods for forming the dielectric layer include vacuum vapor deposition, sol-gel hydrolysis, 5 CVD in a fluidized bed, downstream plasma onto vibrating trays filled with particles, and electrochemical deposition. A suitable SiO<sub>2</sub> sol-gel process is described in U.S. Patent No. 5,858,078 to Andes et al., the disclosure of which is incorporated by reference herein. Other examples of suitable sol-gel coating techniques useful in the present invention are disclosed in U.S. Patent No. 4,756,771 to Brodalla; Zink et al., 10 *Optical Probes and Properties of Aluminosilicate Glasses Prepared by the Sol-Gel Method*, Polym. Mater. Sci. Eng., 61, pp. 204-208 (1989); and McKiernan et al., *Luminescence and Laser Action of Coumarin Dyes Doped in Silicate and Aluminosilicate Glasses Prepared by the Sol-Gel Technique*, J. Inorg. Organomet. Polym., 1(1), pp. 87-103 (1991); with the disclosures of each of these incorporated by 15 reference herein.

Suitable preferred methods for forming the absorber layers include vacuum vapor deposition, and sputtering onto a mechanically vibrating bed of particles, as disclosed in commonly assigned copending patent application Serial No. 09/389,962, filed September 3, 1999, entitled "Methods and Apparatus for Producing Enhanced 20 Interference Pigments," which is incorporated by reference herein in its entirety. Alternatively, the absorber coating may be deposited by decomposition through pyrolysis of metal-organo compounds or related CVD processes which may be carried out in a fluidized bed as described in U.S. Patent Nos. 5,364,467 and 5,763,086 to Schmid et al., the disclosures of which are incorporated by reference herein. If no 25 further grinding is carried out, these methods result in an encapsulated core flake section with dielectric and absorber materials therearound. Various combinations of the above coating processes may be utilized during manufacture of pigment flakes with multiple encapsulating coatings.

In one method of forming the absorber coating, powdered flakes or other 30 coated preflakes are placed on a square-shaped vibrating conveyor coater in a vacuum coating chamber as disclosed in U.S. application Serial No. 09/389,962, discussed above. The vibrating conveyor coater includes conveyor trays which are configured

1 in an overlapping inclined arrangement so that the powdered flakes travel along a  
circulating path within the vacuum chamber. While the flakes circulate along this  
path they are effectively mixed by constant agitation so that exposure to the vaporized  
absorber coating material is uniform. Efficient mixing also occurs at the end of each  
5 conveyor tray as the flakes drop in a waterfall off of one tray and onto the next tray.  
The absorber can be sequentially coated on the flakes as they repeatably move under a  
coating material source.

When using vibrating conveyer trays to coat the absorber, it is important that  
the powdered flakes tumble randomly under the coating material source such as  
10 sputter targets and do not become subject to "metal welding" or sticking. Such metal  
welding or sticking can occur between two flat surfaces of reactive metals when such  
metals are deposited in a vacuum. For example, aluminum has a high propensity to  
stick to itself, whereas chromium does not. Suitable absorber materials can be applied  
as either a single material or as an outer capping layer over an underlying different  
15 absorber material.

Figure 9 depicts a dielectric coated magnetic flake ("DMF") 180 according to  
a further embodiment of the invention. The DMF 180 is a three layer design having a  
generally symmetrical thin film structure with a central magnetic layer and at least  
one dielectric layer on either or both of the opposing major surfaces of the central  
20 magnetic layer. Thus, as shown, DMF 180 includes a magnetic layer 182 sandwiched  
in between a dielectric layer 184 and an opposing dielectric layer 186. By inserting  
the magnetic layer between the dielectric layers, the DMF has increased rigidity and  
durability.

Figure 10 depicts a dielectric coated magnetic particle ("DMP") 200 according  
25 to another embodiment of the invention. The DMP 200 is a two layer design with a  
dielectric layer 202 substantially surrounding and encapsulating a central magnetic  
layer 204.

Each of the layers in the coating structures of DMF 180 and DMP 200 can be  
formed of the same materials and thickness as corresponding layers described in  
30 previous embodiments. For example, the dielectric layer in DMF 180 and DMP 200  
can be formed of the same materials and in the same thickness ranges as taught  
hereinabove for dielectric layer 44 of flake 40, and the magnetic layers in DMF 180

1 and DMP 200 can be formed of the same materials and in the same thickness ranges as taught hereinabove for magnetic layer 22 of flake 20. The DMF 180 and DMP 200 can each be used as a pigment flake or particle, or can be used as a magnetic core section with additional layers applied thereover.

5 Figure 11 depicts a color shifting pigment flake 220 according to another embodiment of the invention which does not use a reflector (with high reflectance, *i.e.*, an optical metal). The flake 220 is a three-layer design having a generally symmetrical multilayer thin film structure on opposing sides of a magnetic core section 222, which can be a DMF or a DMP. Thus, first and second absorber layers  
10 224a and 224b are formed on opposing major surfaces of magnetic core section 222. These layers of flake 220 can be formed by a web coating and flake removal process as described previously.

Figure 11 further depicts an alternative coating structure (with phantom lines) for color shifting flake 220, in which the absorber layer is coated around magnetic  
15 core section 222 in an encapsulation process. Accordingly, absorber layers 224a and 224b are formed as part of a continuous coating layer 224 substantially surrounding the flake structure thereunder.

Thus, pigment flake 220 may be embodied either as a multilayer thin film stack flake or a multilayer thin film encapsulated particle. Suitable materials and  
20 thicknesses for the absorber, dielectric, and magnetic layers of flake 220 are the same as taught hereinabove.

Some flakes of the invention can be characterized as multilayer thin film interference structures in which layers lie in parallel planes such that the flakes have first and second parallel planar outer surfaces and an edge thickness perpendicular to  
25 the first and second parallel planar outer surfaces. Such flakes are produced to have an aspect ratio of at least about 2:1, and preferably about 5-15:1 with a narrow particle size distribution. The aspect ratio of the flakes is ascertained by taking the ratio of the longest planar dimension of the first and second outer surfaces to the edge thickness dimension of the flakes.

30 One presently preferred method of fabricating a plurality of pigment flakes, each of which having the multilayer thin film coating structure of flake 40 shown in Figure 2, is based on conventional web coating techniques used to make optical thin

1 films. Although flake 40 is described hereinbelow, the other flake structures taught  
herein can also be fabricated with a procedure similar to the one described  
hereinbelow. Accordingly, a first absorber layer is deposited on a web of flexible  
material such as polyethylene terephthalate (PET) which has an optional release layer  
5 thereon. The absorber layer can be formed by a conventional deposition process such  
as PVD, CVD, PECVD, sputtering, or the like. The above mentioned deposition  
methods enable the formation of a discrete and uniform absorber layer of a desired  
thickness.

10 Next, a first dielectric layer is deposited on the absorber layer to a desired  
optical thickness by a conventional deposition process. The deposition of the  
dielectric layer can be accomplished by a vapor deposition process (*e.g.*, PVD, CVD,  
PECVD), which results in the dielectric layer cracking under the stresses imposed as  
the dielectric transitions from the vapor into the solid phase.

15 The magnetic core is then deposited. In the case of reflector layers, a first  
reflector layer is then deposited by PVD, CVD, or PECVD on the first dielectric  
layer, taking on the characteristics of the underlying cracked dielectric layer.  
Magnetic layers are then applied by e-beam evaporation, sputtering, electrodeposition,  
or CVD, followed by a second reflector layer being deposited.

20 This is followed by a second dielectric layer being deposited on the second  
reflector layer and preferably having the same optical thickness as the first dielectric  
layer. Finally, a second absorber layer is deposited on the second dielectric layer and  
preferably has the same physical thickness as the first absorber layer.

25 Thereafter, the flexible web is removed, either by dissolution in a preselected  
liquid or by way of a release layer, both of which are well known to those skilled in  
the art. As a result, a plurality of flakes are fractured out along the cracks of the  
layers during removal of the web from the multilayer thin film. This method of  
manufacturing pigment flakes is similar to that more fully described in U.S. Patent  
No. 5,135,812 to Phillips et al., the disclosure of which is incorporated by reference  
herein. The pigment flakes can be further fragmented if desired by, for example,  
30 grinding the flakes to a desired size using an air grind, such that each of the pigment  
flakes has a dimension on any surface thereof ranging from about 2 microns to about  
200 microns.

1        In order to impart additional durability to the color shifting flakes, an  
annealing process can be employed to heat treat the flakes at a temperature ranging  
from about 200- 300°C, and preferably from about 250-275°C, for a time period  
ranging from about 10 minutes to about 24 hours, and preferably a time period of  
5        about 15-60 minutes.

Other pigment flake structures, methods of forming them, and additional  
features compatible therewith can be found in *Phillips '648*, U.S. Patent No.  
4,705,356 to Berning et al., and U.S. Patent No. 6,157,489 to Bradley et al.; U.S.  
Patent Application Nos. 09/685,468 to Phillips et al, 09/715,937 to Coombs et al.,  
10        09/715,934 to Mayer et al., 09/389,962 to Phillips et al., and 09/539,695 to Phillips et  
al., the disclosures of which are each incorporated herein by reference. One skilled in  
the art will recognize, in light of the disclosure herein, that the magnetic layers  
discussed previously can be combined with the coating structures disclosed in the  
above patents and applications, such as by replacing a reflector layer with the RMF or  
15        RMP disclosed herein to obtain additional useful coating structures.

Referring now to Figure 12, pigment flake 240 is deposited according to  
another embodiment of the invention. As illustrated, flake 240 is a multilayer design  
having a generally symmetrical thin film structure on opposing sides of a magnetic  
layer such as a reflective magnetic core 242, which can be any non-color shifting  
20        magnetic pigment flake or particle having reflective properties described herein or  
known in the art. For example, reflective magnetic core 242 can be a single reflective  
magnetic layer such as a monolithic layer of Ni or other magnetic reflective metal, or  
can be a multilayer magnetic structure such as Al/Fe/Al. A first colored layer such as  
selective absorber layer 244a and a second colored layer such as selective absorber  
25        layer 244b are formed on opposing major surfaces of reflective magnetic core 242.  
These colored layers of flake 240 can be formed by a web coating and flake removal  
process as described previously.

Figure 12 further depicts an alternative coating structure (with phantom lines)  
for flake 240, in which a colored layer such as selective absorber layer 244 is coated  
30        around reflective magnetic core 242 in an encapsulation process. Accordingly,  
selective absorber layers 244a and 244b are formed as part of a contiguous coating  
layer 244 substantially surrounding the flake structure thereunder. Suitable

1 encapsulation methods for forming flake 240 are as described in a copending U.S.  
Application Serial No. 09/626,041, filed July 27, 2000, the disclosure of which is  
incorporated by reference herein.

5 Thus, pigment flake 240 may be embodied either as a multilayer thin film  
stack flake or a multilayer thin film encapsulated particle. Suitable materials and  
thicknesses for use in the reflective magnetic core of flake 240 are the same as taught  
hereinabove, so long as both reflective and magnetic properties are maintained.

The colored layers of flake 240 can be formed of a variety of different  
absorbing and/or reflecting materials in one or more layers. Preferably, the colored  
10 layers such as selective absorber layers are formed to have a thickness of from about  
0.05  $\mu\text{m}$  to about 5  $\mu\text{m}$ , and more preferably from about 1  $\mu\text{m}$  to about 2  $\mu\text{m}$ , by  
conventional coating processes for dye stuffs, when an organic dye material is utilized  
to form the selective absorber layers. Preferably, the colored layers are formed to  
have a thickness of from about 0.05  $\mu\text{m}$  to about 0.10  $\mu\text{m}$  when colored metallics or  
15 other inorganic colorant materials are utilized.

Examples of suitable organic dyes that can be used to form the selective  
absorber layers of flake 240 include copper phthalocyanine, perylene-based dyes,  
anthraquinone-based dyes, and the like; azo dyes and azo metal dyes such as  
aluminum red (RLW), aluminum copper, aluminum bordeaux (RL), aluminum fire-  
20 red (ML), aluminum red (GLW), aluminum violet (CLW), and the like; as well as  
combinations or mixtures thereof. Such dyes can be applied by conventional coating  
techniques and even by evaporation.

The colored layers of flake 240 can also be formed of a variety of  
conventional organic or inorganic pigments applied singly or dispersed in a pigment  
25 vehicle. Such pigments are described in the NPIRI Raw Materials Data Handbook,  
Vol. 4, Pigments (1983), the disclosure of which is incorporated by reference herein.

In another embodiment, the selective absorber layers of flake 240 comprise a  
sol-gel matrix holding a colored pigment or dye. For example, the selective absorber  
layer can be formed of aluminum oxide or silicon dioxide applied by a sol-gel  
30 process, with organic dyes absorbed into pores of the sol-gel coating or bound to the  
surface of the coating. Suitable organic dyes used in the sol-gel coating process  
include those available under the trade designations Aluminiumrot GLW (aluminum

1 red GLW) and Aluminiumviolett CLW (aluminum violet CLW) from the Sandoz  
Company. Aluminum red GLW is an azo metal complex containing copper, and  
aluminum violet CLW is a purely organic azo dye. Examples of sol-gel coating  
techniques useful in the present invention are disclosed in the following: U.S. Patent  
5 No. 4,756,771 to Brodalla (1988); Zink et al., Optical Probes and Properties of  
Aluminosilicate Glasses Prepared by the Sol-Gel Method, Polym. Mater. Sci. Eng.,  
61, pp. 204-208 (1989); and McKiernan et al., Luminescence and Laser Action of  
Coumarin Dyes Doped in Silicate and Aluminosilicate Glasses Prepared by the Sol-  
Gel Technique, J. Inorg. Organomet. Polym., 1(1), pp. 87-103 (1991); the disclosures  
10 of all of these are incorporated herein by reference.

In a further embodiment, the colored layers of flake 240 can be formed of an  
inorganic colorant material. Suitable inorganic colorants include selective absorbers  
such as titanium nitride, chromium nitride, chromium oxide, iron oxide, cobalt-doped  
alumina, and the like, as well as colored metallics such as copper, brass, titanium, and  
15 the like.

It should be understood that various combinations of the above dyes,  
pigments, and colorants may also be employed to achieve a desired color  
characteristic for flake 240. The organic dyes, pigments, and colorants discussed  
herein can be used in the invention to achieve pigments with bright colors having  
20 magnetic properties.

Various modifications and combinations of the foregoing embodiments are  
also considered within the scope of the invention. For example, additional dielectric,  
absorber, and/or other optical coatings can be formed around each of the above flake  
or particle embodiments, or on a composite reflective film prior to flake formation, to  
25 yield further desired optical characteristics. Such additional coatings can provide  
additional color effects to the pigments. For example a colored dielectric coating  
added to a color shifting flake would act as a color filter on the flake, providing a  
subtractive color effect which changes the color produced by the flake.

The pigment flakes of the present invention can be interspersed within a  
30 pigment medium to produce a colorant composition which can be applied to a wide  
variety of objects or papers. The pigment flakes added to a medium produces a  
predetermined optical response through radiation incident on a surface of the

1 solidified medium. Preferably, the pigment medium contains a resin or mixture of  
resins which can be dried or hardened by thermal processes such as thermal cross-  
linking, thermal setting, or thermal solvent evaporation or by photochemical cross-  
linking. Useful pigment media include various polymeric compositions or organic  
5 binders such as alkyd resins, polyester resins, acrylic resins, polyurethane resins, vinyl  
resins, epoxies, styrenes, and the like. Suitable examples of these resins include  
melamine, acrylates such as methyl methacrylate, ABS resins, ink and paint  
formulations based on alkyd resins, and various mixtures thereof. The flakes  
combined with the pigment media produce a colorant composition that can be used  
10 directly as a paint, ink, or moldable plastic material. The colorant composition can  
also be utilized as an additive to conventional paint, ink, or plastic materials.

The pigment medium also preferably contains a solvent for the resin. For the  
solvent, generally, either an organic solvent or water can be used. A volatile solvent  
can also be used in the medium. As for the volatile solvent, it is preferable to use a  
15 solvent which is both volatile as well as dilutable, such as a thinner. In particular,  
faster drying of the pigment medium can be achieved by increasing the amount of the  
solvent with a low boiling point composition such as methyl ethyl ketone (MEK).

In addition, the flakes can be optionally blended with various additive  
materials such as conventional pigment flakes, particles, or dyes of different hues,  
20 chroma and brightness to achieve the color characteristics desired. For example, the  
flakes can be mixed with other conventional pigments, either of the interference type  
or noninterference type, to produce a range of other colors. This preblended  
composition can then be dispersed into a polymeric medium such as a paint, ink,  
plastic or other polymeric pigment vehicle for use in a conventional manner.

25 Examples of suitable additive materials that can be combined with the flakes  
of the invention include non-color shifting high chroma or high reflective platelets  
which produce unique color effects, such as  $\text{MgF}_2/\text{Al}/\text{MgF}_2$  platelets, or  $\text{SiO}_2/\text{Al}/\text{SiO}_2$   
platelets. Other suitable additives that can be mixed with the magnetic color shifting  
flakes include lamellar pigments such as multi-layer color shifting flakes, aluminum  
30 flakes, graphite flakes, glass flakes, iron oxide, boron nitride, mica flakes, interference  
based  $\text{TiO}_2$  coated mica flakes, interference pigments based on multiple coated plate-  
like silicatic substrates, metal-dielectric or all-dielectric interference pigments, and the

1 like; and non-lamellar pigments such as aluminum powder, carbon black, ultramarine  
blue, cobalt based pigments, organic pigments or dyes, rutile or spinel based inorganic  
pigments, naturally occurring pigments, inorganic pigments such as titanium dioxide,  
talc, china clay, and the like; as well as various mixtures thereof. For example,  
5 pigments such as aluminum powder or carbon black can be added to control lightness  
and other color properties.

The magnetic color shifting flakes of the present invention are particularly  
suited for use in applications where colorants of high chroma and durability are  
desired. By using the magnetic color shifting flakes in a colorant composition, high  
10 chroma durable paint or ink can be produced in which variable color effects are  
noticeable to the human eye. The color shifting flakes of the invention have a wide  
range of color shifting properties, including large shifts in chroma (degree of color  
purity) and also large shifts in hue (relative color) with a varying angle of view. Thus,  
an object colored with a paint containing the color shifting flakes of the invention will  
15 change color depending upon variations in the viewing angle or the angle of the object  
relative to the viewing eye.

The pigment flakes of the invention can be easily and economically utilized in  
paints and inks which can be applied to various objects or papers, such as motorized  
vehicles, currency and security documents, household appliances, architectural  
20 structures, flooring, fabrics, sporting goods, electronic packaging/housing, product  
packaging, etc. The color shifting flakes can also be utilized in forming colored  
plastic materials, coating compositions, extrusions, electrostatic coatings, glass, and  
ceramic materials.

Generally, the foils of the invention have a nonsymmetrical thin film coating  
25 structure, which can correspond to the layer structures on one side of an RMF in any  
of the above described embodiments related to thin film stack flakes. The foils can be  
laminated to various objects or can be formed on a carrier substrate. The foils of the  
invention can also be used in a hot stamping configuration where the thin film stack  
of the foil is removed from a release layer of a substrate by use of a heat activated  
30 adhesive and applied to a countersurface. The adhesive can be either coated on a  
surface of the foil opposite from the substrate, or can be applied in the form of a UV  
activated adhesive to the surface on which the foil will be affixed.

1        Figure 13 depicts a coating structure of a color shifting foil 300 formed on a  
substrate 302, which can be any suitable material such as a flexible PET web, carrier  
substrate, or other plastic material. A suitable thickness for substrate 302 is, for  
example, about 2 to 7 mils. The foil 300 includes a magnetic layer 304 on substrate  
5        302, a reflector layer 306 on magnetic layer 304, a dielectric layer 308 on reflector  
layer 306, and an absorber layer 310 on dielectric layer 308. The magnetic, reflector,  
dielectric and absorber layers can be composed of the same materials and can have the  
same thicknesses as described above for the corresponding layers in flakes 20 and 40.

10       The foil 300 can be formed by a web coating process, with the various layers  
as described above sequentially deposited on a web by conventional deposition  
techniques to form a thin film foil structure. The foil 300 can be formed on a release  
layer of a web so that the foil can be subsequently removed and attached to a surface  
of an object. The foil 300 can also be formed on a carrier substrate, which can be a  
web without a release layer.

15       Figure 14 illustrates one embodiment of a foil 320 disposed on a web 322  
having an optional release layer 324 on which is deposited a magnetic layer 326, a  
reflector layer 328, a dielectric layer 330, and an absorber layer 332. The foil 320  
may be utilized attached to web 322 as a carrier when a release layer is not employed.  
Alternatively, foil 320 may be laminated to a transparent substrate (not shown) via an  
20       optional adhesive layer 334, such as a transparent adhesive or ultraviolet (UV) curable  
adhesive, when the release layer is used. The adhesive layer 334 is applied to  
absorber layer 332.

25       Figure 15 depicts an alternative embodiment in which a foil 340 having the  
same thin film layers as foil 320 is disposed on a web 322 having an optional release  
layer 324. The foil 340 is formed such that absorber layer 332 is deposited on web  
322. The foil 340 may be utilized attached to web 322 as a carrier, which is  
preferably transparent, when a release layer is not employed. The foil 340 may also  
be attached to a substrate such as a countersurface 342 when the release layer is used,  
via an adhesive layer 334 such as a hot stampable adhesive, a pressure sensitive  
30       adhesive, a permanent adhesive, and the like. The adhesive layer 334 can be applied  
to magnetic layer 326 and/or to countersurface 342.

When a hot stamp application is employed, the optical stack of the foil is

1 arranged so that the optically exterior surface is adjacent the release layer. Thus, for  
example, when foil 340 in Figure 15 is released from web 322, absorber layer 332 is  
optically present on the exterior. In one preferred embodiment, release layer 324 is a  
transparent hardcoat that stays on absorber layer 332 to protect the underlying layers  
5 after transfer from web 322.

Further details of making and using optical stacks as hot stamping foils can be  
found in U.S. Patent Nos. 5,648,165, 5,002,312, 4,930,866, 4,838,648, 4,779,898, and  
4,705,300, the disclosures of which are incorporated by reference herein.

10 Referring now to Figure 16, another embodiment of the invention is depicted  
in the form of an optical article 400 having paired optical structures. The optical  
article 400 includes a substrate 402 having an upper surface 404 and a lower surface  
406. The substrate 402 can be flexible or rigid and can be formed of any suitable  
material such as paper, plastic, cardboard, metal, or the like, and can be opaque or  
transparent. Non-overlapping paired first and second coating structures 408, 410 are  
15 disposed on upper surface 404 so as to overlie non-overlapping first and second  
regions on surface 404. Thus, first and second coating structures 408, 410 are not  
superimposed but are physically separated from each other on surface 404, although  
in an abutting relationship. For example, in one embodiment, first coating structure  
408 can be in the form of a rectangle or square and is disposed within a recess 412  
20 formed by second coating structure 410, also being in the form of a rectangle or  
square that forms a border or frame that surrounds first coating structure 408. Thus,  
when optical article 400 is viewed from above, coating structures 408, 410 can be  
viewed simultaneously.

25 The first coating structure 408 has a first pigment 414 formed of magnetic  
pigment flakes or particles, such as color shifting magnetic flakes, constructed in the  
manner hereinbefore described to provide a magnetic signature. The magnetic  
properties of pigment 414 are provided by a non-optically observable magnetic layer  
within one or more of the magnetic flakes or particles. The second coating structure  
410 has a second pigment 416 formed of non-magnetic pigment flakes or particles,  
30 such as color shifting non-magnetic flakes. Alternatively, the second coating  
structure 410 could be formed to contain the magnetic pigments and the first coating  
structure 408 could be formed to contain the non-magnetic pigments. The pigments

1 414, 416 are dispersed in a solidified liquid pigment vehicle 418, 420 of a conventional type so that the pigments 414, 416 produce the desired optical characteristics. For example, the liquid vehicle can be a conventional ink vehicle or a conventional paint vehicle of a suitable type.

5 In an alternative embodiment, optical article 400 can be formed by using a suitable magnetic foil structure, such as the color shifting magnetic foils disclosed hereinabove, in place of coating structure 408, and by using a non-magnetic foil structure such as a conventional color shifting foil in place of coating structure 410. The magnetic properties of the magnetic foil structure are thus provided by a  
10 magnetic layer which is not optically observable. Non-overlapping paired first and second foil structures, one magnetic and one non-magnetic, would be disposed on upper surface 404 of substrate 402 so as to overlie non-overlapping first and second regions on surface 404.

15 Other optical articles with paired optically variable structures, which could be modified to include magnetic layers in one of the paired structures such as disclosed herein, are taught in U.S. Patent No. 5,766,738 to Phillips et al., the disclosure of which is incorporated by reference herein.

Referring now to Figure 17, another embodiment of the invention is depicted in the form of an optical article 450 having overlapping paired optical structures. The  
20 optical article 450 includes a substrate 452 having an upper surface region 454. The substrate 452 can be formed of the same materials as described for substrate 402 shown in Figure 16. A magnetic pigment coating structure 456 overlies upper surface region 454 of substrate 452. The magnetic pigment coating structure 456 includes a plurality of multilayer magnetic pigments 458, such as those described previously,  
25 which are dispersed in a solidified pigment vehicle. The magnetic properties of the pigment coating structure 456 are provided by a non-optically observable magnetic layer within each of the multilayer magnetic pigments 458. A non-magnetic pigment coating structure 460 overlies at least a portion of magnetic pigment coating structure 456. The non-magnetic pigment coating structure 460 includes a plurality of non-  
30 magnetic pigments 462 dispersed in a solidified pigment vehicle.

In an alternative embodiment of optical article 450, a non-magnetic pigment coating structure can be used in place of magnetic pigment coating structure 456

1 overlying upper surface region 454 of substrate 452. A magnetic pigment coating structure is then used in place of non-magnetic pigment coating structure 460.

5 In a further alternative embodiment, optical article 450 can be formed by using a suitable magnetic foil structure, such as the color shifting magnetic foils disclosed hereinabove, in place of coating structure 456. A non-magnetic foil structure such as a conventional color shifting foil is then used in place of coating structure 460. Alternatively, a non-magnetic foil structure can be used in place of coating structure 456, and a magnetic foil structure is then used in place of coating structure 460.

10 The respective pigment coating or foil structures in optical articles 400 or 450 can be selected to provide identical coloring or identical color shifting effects to articles 400 and 450, or can be selected to provide different colors or different color shifting effects. Of course, one skilled in the art will recognize that a variety of combinations of optical features can be used by selecting appropriate coatings or foils with the desired optical characteristics to add various security features to optical articles 400 and 450.

15 Although the pigment coating or foil structures used in articles 400 and 450 may have substantially the same color or color effects, *e.g.*, the same color shifting effects, only one of the pigment coating or foil structures in the articles carries a covert magnetic signature. Therefore, although a human eye cannot detect the magnetic features of the pigment coating or foil structure, a magnetic detection system such as a Faraday rotator detector can be used to detect the magnetic covert signature in the pigment or foil and any information magnetically encoded therein.

20 From the foregoing it can be seen that there have been provided thin film structures which have both magnetic, and optionally, color shifting properties, which have many different types of applications, particularly where additional security is desired.

25 For example, a structure or device formed with the pigments of the invention can be placed in a bar code pattern which would produce a color shifting bar code device that can appear on a label or on an article itself. Such a bar code would function as a color shifting bar code that could be read by both optical and magnetic readers. Such a bar code color shifting device would provide three security features, the bar code itself, the color shifting characteristic, and the magnetic characteristic. In

1 addition, information can be encoded in the magnetic layers of the pigments of the  
invention. For example, the magnetic layers could record typical information which  
is carried by a credit card in a magnetic stripe. In addition, pigments of the invention  
could be utilized for putting the numbers on the bottoms of checks so that the  
5 information carried by the check could be read magnetically as with present day  
checks while also providing an optical variable feature.

The following examples are given to illustrate the present invention, and are  
not intended to limit the scope of the invention.

#### Example 1

10 A three layer magnetic coating sample was prepared with 1000 Å Aluminum,  
1000 Å Iron, and 1000 Å Aluminum (Al/Fe/Al). The coating sample was prepared in  
a roll coater, using a 2 mil polyester web coated with an organic release layer (soluble  
in acetone). After stripping the three layer coating from the web to form pigment  
flake particles, the particles were filtered and sized by exposing the particles in  
15 isopropyl alcohol to ultrasonic agitation for 5 minutes using a Branson sonic welder.  
Particle size was determined using a Horiba LA-300 particle sizing instrument (laser  
scattering based system). The mean particle size was determined to be 44 µm (22 µm  
standard deviation) in the planar dimension, with a gaussian distribution. Following  
the sizing, the pigment particles were filtered and dried.

20 A dry weight of magnetic pigment to binder (Du Pont auto refinish paint  
vehicle) in the ratio of 1:4 was drawn down onto a thin cardboard sheet (Leneta card).  
A "draw-down" is a paint or ink sample spread on paper to evaluate the color.  
Typically, a draw-down is formed with the edge of a putty knife or spatula by  
"drawing down" a small glob of paint or ink to get a thin film of the paint or ink.  
25 Alternatively, the draw-down is made using a Mayer rod pulled across a Leneta card  
and through a small glob of paint. A conventional sheet magnet was placed  
underneath the card while the drawing down was occurring and left in place until the  
paint vehicle dried. The result of the magnetic fields on this pigment sample was to  
create parallel bright and dark areas in the pigment. By using an ultra small area  
30 viewer (USAV, 2.3 mm) on a SF-600 DataColor spectrophotometer, the bright  
aluminum areas of the pigment sample had a reflective luminance, Y, of 53% whereas  
the dark areas had a reflective luminance of 43%. However, it was difficult to fit the

1 aperture within the dark and bright lines suggesting that the difference in brightness  
may actually be larger than these measurements.

#### Example 2

5 A magnetic ink sample was prepared by mixing a 0.5 g sample of the  
magnetic pigment of Example 1 (Al/Fe/Al) with 3.575 g of standard Intaglio ink  
vehicle (high viscosity ink vehicle) and 0.175 g of an ink dryer. The ink sample was  
drawn down onto paper using a flat putty knife. A magnetic strip with the word  
"FLEX" cut out from it was placed beneath the paper during the drawing down step.  
10 The pattern of the magnetic lines in the dried magnetic ink was readily visible as  
black and white (silver color) strips with the word "FLEX" readily apparent. The  
optical image of the word "FLEX" in the ink sample was visible at normal incidence  
and at approximately a 45 degree angle of viewing.

#### Example 3

15 A magnetic ink sample was prepared as in Example 2 using an Intaglio ink  
vehicle and coated over paper having a sheet magnet placed behind it. The magnet  
had a cut out of a stylized letter "F." In addition to the magnetic pigment (Al/Fe/Al)  
orienting along the magnetic field lines, the cut out "F" was embossed upward away  
from the paper and was bright silver in appearance. The "F" stood out over the  
surrounding area by about 6 microns. This was caused by the paper pushed slightly  
20 into the "F" recess of the magnet by the force of the putty knife drawing down the  
highly viscous Intaglio ink. After the paper relaxed, the "F" area remained bright with  
the Al/Fe/Al flakes oriented parallel to the surface of the paper but in a stepped-up  
height above the surrounding coating.

#### Example 4

25 A stylized letter "F" was cut out of a flexible sheet magnet using an exacto  
knife. A draw-down card was placed on top of and in contact with the sheet magnet.  
A magnetic color shifting pigment according to the invention was mixed with an  
acrylic resin based vehicle and applied to the card with a #22 wire metering rod. The  
resultant draw-down had striped superimposed black lines that replicated the field  
30 pattern outside of the stylized "F" in the sheet magnet below the card. The entire  
surface of the drawn-down card exhibited color shifting effects. Where the pattern of  
the stylized "F" was observed, the stylized "F" only had color shifting effects, while

1 the background had both color shifting effects and the superimposed black lines.

The cut out stylized letter "F" pieces from the sheet magnet were used in another draw-down with the same magnetic pigment and vehicle described previously in this example. The resultant draw-down had striped superimposed black lines that replicated the field pattern within the cutout stylized "F" magnet pieces. The entire surface of the drawn-down exhibited a color shifting effect. Where the pattern of the stylized "F" was observed, the stylized "F" had both color shifting effects and the superimposed black lines, while the background had only color shifting effects.

10 Thus, in both instances the entire surface of the draw-down cards exhibited color shifting effects, while the areas directly above the magnets additionally had superimposed striped black lines due to the magnetic field pattern.

The present invention may be embodied in other specific forms without departing from its spirit or essential characteristics. The described embodiments are to be considered in all respects only as illustrative and not restrictive. The scope of the invention is, therefore, indicated by the appended claims rather than by the foregoing description. All changes which come within the meaning and range of equivalency of the claims are to be embraced within their scope.

What is claimed is:

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- 1 1. A magnetic pigment flake, comprising:
- 2 a central magnetic layer having a first major surface, an opposing
- 3 second major surface, and at least one side surface;
- 4 a first reflector layer on the first major surface of the magnetic layer;
- 5 and
- 6 a second reflector layer on the second major surface of the magnetic
- 7 layer;
- 8 wherein the pigment flake exhibits a reflectivity corresponding to the
- 9 reflectivity of the reflector layers and exhibits magnetic characteristics based on the
- 10 relative magnetism of the magnetic layer.
- 11 2. The pigment flake of claim 1, wherein the first and second reflector
- 12 layers are on each of the first and second major surfaces but not on the at least one
- 13 side surface of the magnetic layer.
- 14 3. The pigment flake of claim 2, further comprising a first dielectric layer
- 15 on the first reflector layer and a second dielectric layer on the second reflector layer.
- 16 4. The pigment flake of claim 3, wherein the first and second dielectric
- 17 layers are selectively absorbing and provide additional color effects to the pigment
- 18 flake.
- 19 5. The pigment flake of claim 2, further comprising a dielectric layer
- 20 substantially surrounding the first and second reflector layers and the magnetic layer.
- 21 6. The pigment flake of claim 5, wherein the dielectric layer is selectively
- 22 absorbing and provides additional color effects to the pigment flake.
- 23 7. The pigment flake of claim 1, wherein the first and second reflector
- 24 layers form part of a contiguous reflecting layer substantially surrounding the
- 25 magnetic layer.
- 26 8. The pigment flake of claim 7, further comprising a dielectric layer
- 27 substantially surrounding the reflecting layer.
- 28 9. The pigment flake of claim 8, wherein the dielectric layer is selectively
- 29 absorbing and provides additional color effects to the pigment flake.
- 30 10. The pigment flake of claim 1, wherein the magnetic layer comprises a
- 31 soft magnetic material.
- 32 11. The flake of claim 1, wherein the magnetic layer is composed of a

1 material with a coercivity of less than about 2000 Oe.

12. The flake of claim 1, wherein the magnetic layer is composed of a material with a coercivity of less than about 300 Oe.

5 13. The pigment flake of claim 1, wherein the magnetic layer comprises a material selected from the group consisting of iron, nickel, cobalt, iron, gadolinium, terbium, dysprosium, erbium, and alloys or oxides thereof.

14. The pigment flake of claim 1, wherein the magnetic layer comprises a material selected from the group consisting of Fe/Si, Fe/Ni, FeCo, Fe/Ni/Mo, and combinations thereof.

10 15. The pigment flake of claim 1, wherein the magnetic layer comprises a hard magnetic material.

16. The pigment flake of claim 1, wherein the magnetic layer comprises a material selected from the group consisting of SmCo<sub>5</sub>, NdCo<sub>5</sub>, Sm<sub>2</sub>Co<sub>17</sub>, Nd<sub>2</sub>Fe<sub>14</sub>B, TbFe<sub>2</sub>, and combinations thereof.

15 17. The pigment flake of claim 1, wherein the magnetic layer comprises a material selected from the group consisting of Fe<sub>3</sub>O<sub>4</sub>, NiFe<sub>2</sub>O<sub>4</sub>, MnFe<sub>2</sub>O<sub>4</sub>, CoFe<sub>2</sub>O<sub>4</sub>, YIG, GdIG, and combinations thereof.

18. The pigment flake of claim 1, wherein the magnetic layer has a physical thickness of about 200 Å to about 10,000 Å.

20 19. The pigment flake of claim 1, wherein the reflector layers comprise a reflective material selected from the group consisting of aluminum, silver, copper, gold, platinum, tin, titanium, palladium, nickel, cobalt, rhodium, niobium, chromium, and combinations or alloys thereof.

25 20. The pigment flake of claim 1, wherein the reflector layers each have a physical thickness of about 400 Å to about 2,000 Å.

21. A magnetic colorant composition, comprising:  
a pigment medium; and

30 a plurality of pigment flakes dispersed in the pigment medium, the pigment flakes having a multilayer structure substantially the same as the pigment flake defined in claim 1.

22. The colorant composition of claim 21, wherein the pigment medium comprises a material selected from the group consisting of acrylic melamine,

1 urethanes, polyesters, vinyl resins, acrylates, methyl methacrylate, ABS resins,  
epoxies, styrenes, ink and paint formulations based on alkyd resins, and mixtures  
thereof.

23. A magnetic color shifting pigment flake, comprising:  
5 a magnetic core section including:  
a central magnetic layer having a first major surface, an  
opposing second major surface, and at least one side surface; and  
a first reflector layer on the first major surface of the magnetic  
layer, and an opposing second reflector layer on the second major  
10 surface of the magnetic layer;  
a first dielectric layer overlying the first reflector layer, and a second  
dielectric layer overlying the second reflector layer; and  
a first absorber layer overlying the first dielectric layer, and a second  
absorber layer overlying the second dielectric layer;  
15 wherein the pigment flake exhibits a discrete color shift such that the pigment  
flake has a first color at a first angle of incident light or viewing and a second color  
different from the first color at a second angle of incident light or viewing.

24. The pigment flake of claim 23, wherein the magnetic layer comprises a  
soft magnetic material.

20 25. The pigment flake of claim 23, wherein the magnetic layer comprises a  
material selected from the group comprising iron, nickel, cobalt, iron, gadolinium,  
terbium, dysprosium, erbium, and alloys or oxides thereof.

26. The pigment flake of claim 23, wherein the magnetic layer comprises a  
material selected from the group consisting of Fe/Si, Fe/Ni, FeCo, Fe/Ni/Mo, and  
25 combinations thereof.

27. The pigment flake of claim 23, wherein the magnetic layer comprises a  
hard magnetic material.

28. The pigment flake of claim 23, wherein the magnetic layer comprises  
a material selected from the group consisting of SmCo<sub>5</sub>, NdCo<sub>5</sub>, Sm<sub>2</sub>Co<sub>17</sub>, Nd<sub>2</sub>Fe<sub>14</sub>B,  
30 TbFe<sub>2</sub>, and combinations thereof.

29. The pigment flake of claim 23, wherein the magnetic layer comprises  
a material selected from the group consisting of Fe<sub>3</sub>O<sub>4</sub>, NiFe<sub>2</sub>O<sub>4</sub>, MnFe<sub>2</sub>O<sub>4</sub>, CoFe<sub>2</sub>O<sub>4</sub>,

1 YIG, GdIG, and combinations thereof.

30. The pigment flake of claim 23, wherein the reflector layers comprise a reflective material selected from the group consisting of aluminum, silver, copper, gold, platinum, tin, titanium, palladium, nickel, cobalt, rhodium, niobium, chromium,  
5 and combinations or alloys thereof.

31. The pigment flake of claim 23, wherein the first and second dielectric layers comprise a dielectric material having an index of refraction of about 1.65 or less.

32. The pigment flake of claim 23, wherein the dielectric material is  
10 selected from the group consisting of silicon dioxide, aluminum oxide, magnesium fluoride, aluminum fluoride, cerium fluoride, lanthanum fluoride, neodymium fluoride, samarium fluoride, barium fluoride, calcium fluoride, lithium fluoride, and combinations thereof.

33. The pigment flake of claim 23, wherein the first and second dielectric  
15 layers comprise a dielectric material having an index of refraction of greater than about 1.65.

34. The pigment flake of claim 23, wherein the dielectric material is selected from the group consisting of zinc sulfide, zinc oxide, zirconium oxide, titanium dioxide, diamond-like carbon, indium oxide, indium-tin-oxide, tantalum  
20 pentoxide, cerium oxide, yttrium oxide, europium oxide, iron oxides, hafnium nitride, hafnium carbide, hafnium oxide, lanthanum oxide, magnesium oxide, neodymium oxide, praseodymium oxide, samarium oxide, antimony trioxide, silicon monoxide, selenium trioxide, tin oxide, tungsten trioxide, and combinations thereof.

35. The pigment flake of claim 23, wherein the first and second dielectric  
25 layers have an optical thickness in a range from about 2 QWOT at a design wavelength of about 400 nm to about 9 QWOT at a design wavelength of about 700 nm.

36. The pigment flake of claim 23, wherein the first and second dielectric layers have substantially the same optical thickness.

30 37. The pigment flake of claim 23, wherein the first and second dielectric layers are composed of the same material.

38. The pigment flake of claim 23, wherein the first and second dielectric

1 layers are each composed of a dielectric optical stack having a plurality of alternating layers of a high index material and a low index material.

39. The pigment flake of claim 38, wherein the dielectric optical stack has a gradient index of refraction.

5 40. The pigment flake of claim 23, wherein the first and second dielectric layers are each composed of a mixture or multiple sublayers of dielectric materials selected from the group consisting of low index materials, high index materials, and combinations thereof.

10 41. The pigment flake of claim 23, wherein the first and second absorber layers comprise materials that are uniformly absorbing in the visible part of the electromagnetic spectrum.

42. The pigment flake of claim 23, wherein the first and second absorber layers comprise materials that are non-uniformly absorbing in the visible part of the electromagnetic spectrum.

15 43. The pigment flake of claim 23, wherein the first and second absorber layers comprise an absorbing material selected from the group consisting of chromium, nickel, aluminum, silver, copper, palladium, platinum, titanium, vanadium, cobalt, iron, tin, tungsten, molybdenum, rhodium, niobium, carbon, graphite, silicon, germanium, and compounds, mixtures, or alloys thereof.

20 44. The pigment flake of claim 23, wherein the first and second absorber layers comprise an absorbing material selected from the group consisting of metal oxides, metal sulfides, metal carbides, and combinations thereof.

45. The pigment flake of claim 23, wherein the first and second absorber layers each have a physical thickness of about 30 Å to about 500 Å.

25 46. The pigment flake of claim 23, wherein the first and second absorber layers have substantially the same physical thickness.

47. The pigment flake of claim 23, wherein the first and second absorber layers are composed of the same material.

30 48. The pigment flake of claim 23, wherein the first and second reflector layers are on each of the first and second major surfaces but not on the at least one side surface of the magnetic layer.

49. The pigment flake of claim 23, wherein the first and second reflector

1 layers form part of a contiguous reflecting layer substantially surrounding the magnetic layer.

50. The pigment flake of claim 23, wherein the first and second absorber  
5 layers form part of a contiguous absorbing layer substantially surrounding the first and second dielectric layers and the magnetic core section.

51. The pigment flake of claim 23, wherein the first and second absorber layers form part of a contiguous absorbing layer substantially surrounding the first and second dielectric layers, and the first and second dielectric layers form a part of a contiguous dielectric layer substantially surrounding the magnetic core section.

10 52. A magnetic color shifting pigment composition comprising a plurality of color shifting pigment flakes, each of the pigment flakes having a multilayer structure substantially the same as the pigment flake defined in claim 23.

53. A magnetic color-shifting colorant composition, comprising:  
a pigment medium; and  
15 a plurality of color-shifting pigment flakes dispersed in the pigment medium, the pigment flakes having a multilayer structure substantially the same as the pigment flake defined in claim 23.

54. The colorant composition of claim 53, wherein the pigment medium comprises a material selected from the group consisting of acrylic melamine, urethanes, polyesters, vinyl resins, acrylates, methyl methacrylate, ABS resins, epoxies, styrenes, ink and paint formulations based on alkyd resins, and mixtures thereof.

55. The colorant composition of claim 53, wherein the pigment medium is a paint or ink vehicle.

25 56. The colorant composition of claim 53, wherein the pigment flakes have a dimension on any surface thereof ranging from about 2 microns to about 200 microns.

57. The colorant composition of claim 53, wherein the pigment flakes have an aspect ratio of at least about 2 to 1.

30 58. The colorant composition of claim 53, further comprising a plurality of non- color-shifting pigment flakes dispersed in the pigment medium.

- 1        59.        A magnetic pigment flake, comprising:  
                 a central support layer having a first major surface, an opposing second  
                 major surface, and at least one side surface;  
                 a first magnetic layer on the first major surface of the support layer;  
5        and  
                 a second magnetic layer on the second major surface of the support  
                 layer;  
                 wherein the pigment flake exhibits magnetic characteristics based on the  
                 relative magnetism of the magnetic layers.
- 10        60.        The pigment flake of claim 59, wherein the support layer comprises a  
                 dielectric material.
61.        The pigment flake of claim 60, wherein the dielectric material is  
                 selected from the group consisting of mica, coated mica, micaeous iron oxide, glass,  
                 talc, silicon dioxide, boron nitride, boron carbide, alumina, carbon, graphite, bismuth  
15        oxychloride, and combinations thereof.
62.        The pigment flake of claim 59, wherein the first and second magnetic  
                 layers are on each of the first and second major surfaces but not on the at least one  
                 side surface of the support layer.
- 20        63.        The pigment flake of claim 62, further comprising a first dielectric  
                 layer on the first magnetic layer and a second dielectric layer on the second magnetic  
                 layer.
64.        The pigment flake of claim 63, wherein the first and second dielectric  
                 layers are selectively absorbing and provide additional color effects to the pigment  
                 flake.
- 25        65.        The pigment flake of claim 59, wherein the first and second magnetic  
                 layers form part of a contiguous magnetic layer substantially surrounding the support  
                 layer.
66.        The pigment flake of claim 65, further comprising a dielectric layer  
                 substantially surrounding the contiguous magnetic layer.
- 30        67.        The pigment flake of claim 66, wherein the dielectric layer is  
                 selectively absorbing and provides additional color effects to the pigment flake.
68.        The pigment flake of claim 66, further comprising an absorber layer

1 substantially surrounding the dielectric layer.

69. The pigment flake of claim 68, wherein the dielectric layer is selectively absorbing and provides additional color effects to the pigment flake.

5 70. The pigment flake of claim 68, further comprising a reflector layer interposed between the magnetic layer and the dielectric layer.

71. The pigment flake of claim 59, wherein the magnetic layers comprise a soft magnetic material.

72. The pigment flake of claim 59, wherein the magnetic layers are composed of a material with a coercivity of less than about 2000 Oe.

10 73. A magnetic colorant composition, comprising:  
a pigment medium; and

a plurality of pigment flakes dispersed in the pigment medium, the pigment flakes having a multilayer structure substantially the same as the pigment flake defined in claim 59.

15 74. The colorant composition of claim 73, wherein the pigment medium is a paint or ink vehicle.

75. A magnetic pigment flake, comprising:

a central magnetic layer having a first major surface, an opposing second major surface, and at least one side surface;

20 a first dielectric layer on the first major surface of the magnetic layer;  
and

a second dielectric layer on the second major surface of the magnetic layer;

25 wherein the dielectric layers provide increased rigidity, durability, and corrosion resistance to the pigment flake, with the pigment flake exhibiting magnetic characteristics based on the relative magnetism of the magnetic layer.

76. The pigment flake of claim 75, wherein the first and second dielectric layers are selectively absorbing and provide additional color effects to the pigment flake.

30 77. The pigment flake of claim 75, wherein the magnetic layer comprises a soft magnetic material.

78. The pigment flake of claim 75, wherein the magnetic layer is

1 composed of a material with a coercivity of less than about 2000 Oe.

79. The pigment flake of claim 75, wherein the first and second dielectric layers are on each of the first and second major surfaces but not on the at least one side surface of the magnetic layer.

5 80. The pigment flake of claim 79, further comprising a first absorber layer on the first dielectric layer and a second absorber layer on the second dielectric layer.

81. The pigment flake of claim 79, further comprising an absorber layer substantially surrounding the first and second dielectric layers and the magnetic layer.

10 82. The pigment flake of claim 75, wherein the first and second dielectric layers form part of a contiguous dielectric layer substantially surrounding the magnetic layer.

83. The pigment flake of claim 82, wherein the contiguous dielectric layer is selectively absorbing and provides additional color effects to the pigment flake.

15 84. The pigment flake of claim 82, further comprising an absorber layer substantially surrounding the flake.

85. A color shifting pigment flake, comprising:

a magnetic core section having a top surface, a bottom surface, and at least one side surface;

20 a dielectric layer on the top surface and the bottom surface but not on the at least one side surface of the magnetic core section; and an absorber layer substantially surrounding the dielectric layer and in contact with the at least one side surface of the magnetic core section.

86. The pigment flake of claim 85, wherein the magnetic core section includes a magnetic layer.

25 87. The pigment flake of claim 85, wherein the magnetic core section comprises:

a central magnetic layer having a first major surface, an opposing second major surface, and at least one side surface; and

30 a first reflector layer on the first major surface of the magnetic layer, and an opposing second reflector layer on the second major surface of the magnetic layer.

88. The pigment flake of claim 87, wherein the first and second reflector

1 layers are on each of the first and second major surfaces but not on the at least one side surface of the magnetic layer.

89. The pigment flake of claim 87, wherein the first and second reflector  
5 layers form part of a contiguous reflecting layer substantially surrounding the magnetic layer.

90. A magnetic pigment flake, comprising:  
a magnetic core having a first major surface, an opposing second major  
surface, and at least one side surface;  
10 a first colored layer on the first major surface of the magnetic core; and  
a second colored layer on the second major surface of the magnetic  
core.

91. The pigment flake of claim 90, wherein the magnetic core comprises a monolithic magnetic layer.

92. The pigment flake of claim 90, wherein the magnetic core comprises a  
15 multilayer magnetic structure.

93. The pigment flake of claim 92, wherein the multilayer magnetic structure comprises the coating structure Al/Fe/Al.

94. The pigment flake of claim 90, wherein the first and second colored  
20 layers are on each of the first and second major surfaces but not on the at least one side surface of the magnetic core.

95. The pigment flake of claim 90, wherein the first and second colored layers form part of a contiguous colored layer substantially surrounding the magnetic core.

96. The pigment flake of claim 90, wherein the first and second colored  
25 layers comprise an organic dye.

97. The pigment flake of claim 96, wherein the organic dye is selected from the group consisting of copper phthalocyanine, perylene-based dyes, anthraquinone-based dyes, azo dyes, azo metal dyes, and combinations thereof.

98. The pigment flake of claim 96, wherein the colored layers each have a  
30 physical thickness of about 0.05  $\mu\text{m}$  to about 5  $\mu\text{m}$ .

99. The pigment flake of claim 90, wherein the first and second colored layers comprise an inorganic colorant material.

1           100. The pigment flake of claim 99, wherein the inorganic colorant material is selected from the group consisting of titanium nitride, chromium nitride, chromium oxide, iron oxide, cobalt-doped alumina, colored metallics, and combinations thereof.

5           101. The pigment flake of claim 99, wherein the colored layers each have a physical thickness of about 0.05  $\mu\text{m}$  to about 0.10  $\mu\text{m}$ .

          102. The pigment flake of claim 90, wherein the first and second colored layers comprise a sol-gel matrix holding a colored pigment or dye.

          103. A color shifting foil device, comprising:  
              a magnetic layer;  
10           a reflector layer overlying the magnetic layer;  
              a dielectric layer overlying the reflector layer; and  
              an absorber layer overlying the dielectric layer;

              wherein the foil exhibits a discrete color shift such that the foil has a first color at a first angle of incident light or viewing and a second color different from the first  
15           color at a second angle of incident light or viewing.

          104. The foil of claim 103, wherein the magnetic layer comprises a soft magnetic material or a hard magnetic material.

          105. The foil of claim 103, further comprising a web carrier with either the magnetic layer or the absorber layer deposited on the web carrier.

20           106. The foil of claim 105, wherein the web carrier further comprises a release layer thereon disposed between the web carrier and the magnetic layer, or the web carrier and the absorber layer.

          107. The foil of claim 105, further comprising an adhesive layer for laminating the foil to a substrate.

25           108. The foil of claim 107, wherein the adhesive layer is selected from the group consisting of a hot stampable adhesive, a pressure sensitive adhesive, a permanent adhesive, a transparent adhesive, and a UV curable adhesive.

          109. The foil of claim 107, wherein the adhesive layer is overlying the magnetic layer or the absorber layer.

30           110. An optical article comprising:  
              a substrate having first and second non-overlapping regions on a surface of the substrate;

1           a magnetic pigment coating structure overlying the first region, the  
magnetic pigment coating structure including a plurality of multilayer  
magnetic pigments dispersed in a solidified pigment vehicle, the magnetic  
properties of the pigment coating structure being provided by a non-optically  
5       observable magnetic layer within each of the multilayer magnetic pigments;  
and

          a non-magnetic pigment coating structure overlying the second region,  
the non-magnetic pigment coating structure including a plurality of multilayer  
non-magnetic pigments dispersed in a solidified pigment vehicle.

10       111. The article of claim 110, wherein the non-magnetic pigment coating  
structure has a substantially identical color as the magnetic pigment coating structure.

          112. The article of claim 110, wherein one or both of the magnetic pigment  
and non-magnetic pigment coating structures have discrete color shifting effects.

15       113. The article of claim 110, wherein the magnetic pigment and non-  
magnetic pigment coating structures have substantially identical color shifting effects.

          114. The article of claim 110, wherein the magnetic pigment and non-  
magnetic pigment coating structure have different color shifting effects.

          115. An optical article comprising:

          a substrate having an upper surface region;

20       a magnetic pigment coating structure overlying the upper surface  
region of the substrate, the magnetic pigment coating structure including a  
plurality of multilayer magnetic pigments dispersed in a solidified pigment  
vehicle, the magnetic properties of the pigment coating structure being  
provided by a non-optically observable magnetic layer within each of the  
25       multilayer magnetic pigments; and

          a non-magnetic pigment coating structure overlying at least a portion  
of the magnetic pigment coating structure, the non-magnetic pigment coating  
structure including a plurality of non-magnetic pigments dispersed in a  
solidified pigment vehicle.

30       116. The article of claim 115, wherein the non-magnetic pigment coating  
structure has a substantially identical color as the magnetic pigment coating structure.

          117. The article of claim 115, wherein one or both of the magnetic pigment

1 and non-magnetic pigment coating structures have discrete color shifting effects.

118. The article of claim 115, wherein the magnetic pigment and non-magnetic pigment coating structures have substantially identical color shifting effects.

5 119. An optical article comprising:

a substrate having an upper surface region;

a non-magnetic pigment coating structure overlying the upper surface region of the substrate, the non-magnetic pigment coating structure including a plurality of non-magnetic pigments dispersed in a solidified pigment vehicle; and

10 a magnetic pigment coating structure overlying the magnetic pigment coating structure including a plurality of multilayer magnetic pigments dispersed in a solidified pigment vehicle, the magnetic properties of the pigment coating structure being provided by a non-optically observable magnetic layer within each of the multilayer magnetic pigments.

15 120. The article of claim 119, wherein the non-magnetic pigment coating structure has a substantially identical color as the magnetic pigment coating structure.

121. The article of claim 119, wherein one or both of the magnetic pigment and non-magnetic pigment coating structures have discrete color shifting effects.

20 122. The article of claim 119, wherein the magnetic pigment and non-magnetic pigment coating structures have substantially identical color shifting effects.

123. An optical article comprising:

a substrate having first and second non-overlapping regions on a surface of the substrate;

25 a multilayer magnetic foil structure overlying the first region, the magnetic properties of the foil structure provided by a magnetic layer which is not optically observable; and

a non-magnetic foil structure overlying the second region.

124. The article of claim 123, wherein the non-magnetic foil structure has a substantially identical color as the magnetic foil structure.

30 125. The article of claim 123, wherein one or both of the magnetic foil structure and the non-magnetic foil structure have discrete color shifting effects.

126. The article of claim 123, wherein the magnetic foil structure and the

1 non-magnetic foil structure have substantially identical color shifting effects.

127. The article of claim 123, wherein the magnetic foil structure and the non-magnetic foil structure have different color shifting effects.

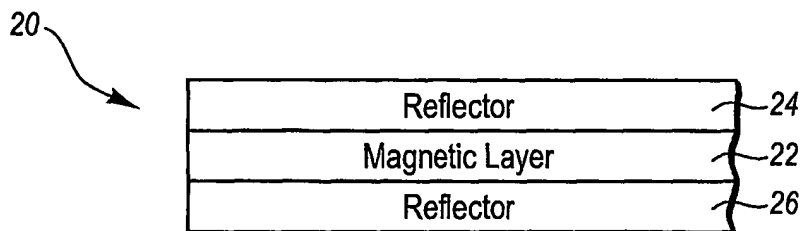
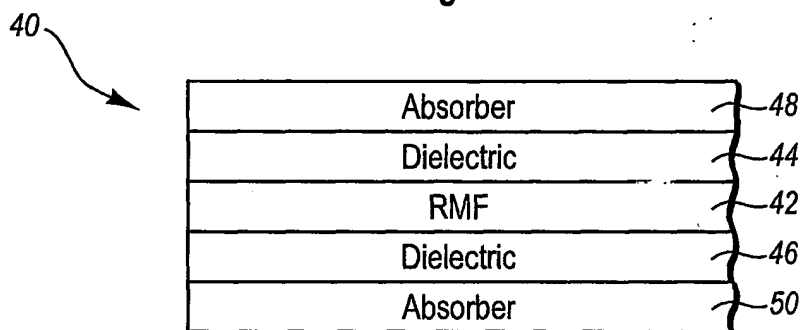
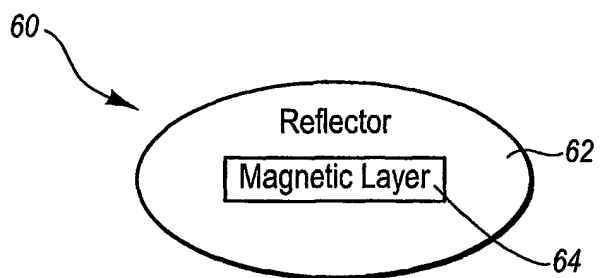
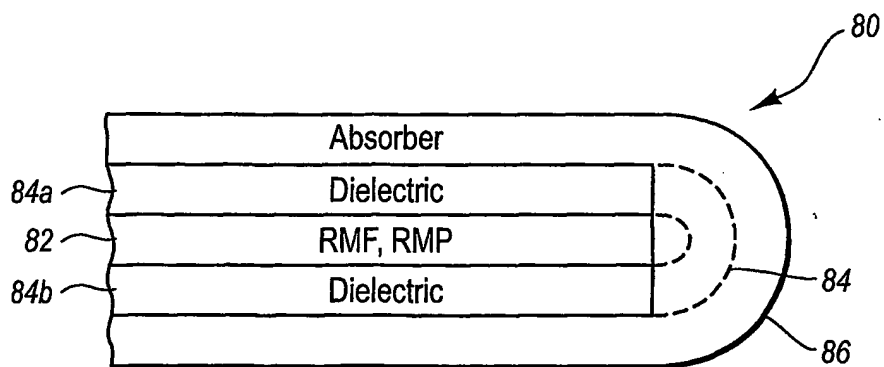
5 128. An optical article comprising:  
a substrate having an upper surface region;  
a multilayer magnetic foil structure overlying the upper surface region of the substrate, the magnetic properties of the magnetic foil structure provided by a magnetic layer which is not optically observable; and  
10 a non-magnetic foil structure overlying at least a portion of the magnetic foil structure.

129. An optical article comprising:  
a substrate having an upper surface region;  
a non-magnetic foil structure overlying the upper surface region of the substrate; and  
15 a multilayer magnetic foil structure overlying at least a portion of the non-magnetic foil structure, the magnetic properties of the magnetic foil structure provided by a magnetic layer which is not optically observable.

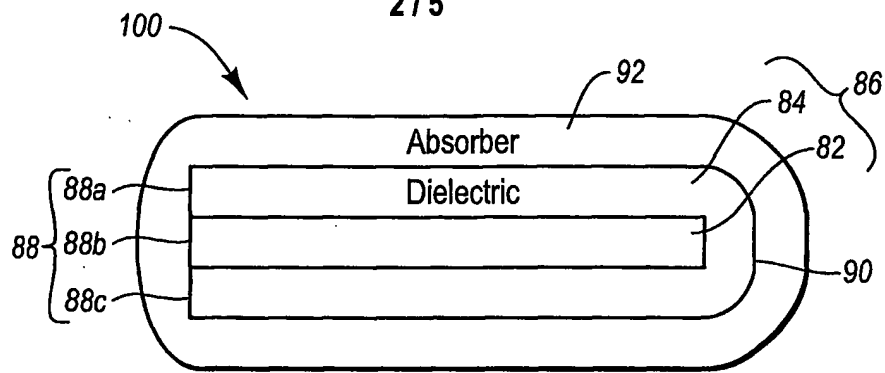
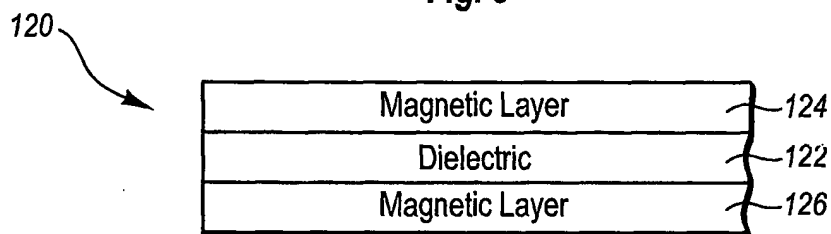
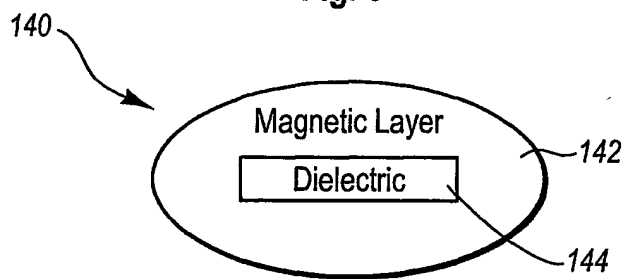
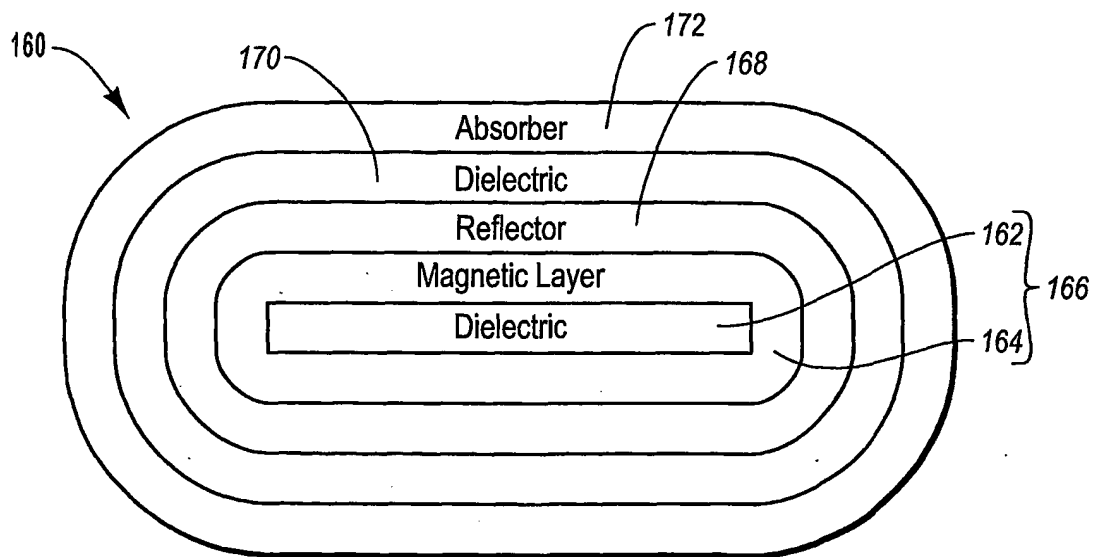
20 130. A magnetic pigment flake, comprising:  
a magnetic core section including:  
a central magnetic layer having a first major surface, an opposing second major surface, and at least one side surface; and  
a first reflector layer on the first major surface of the magnetic layer, and an opposing second reflector layer on the second major surface of the magnetic layer; and  
25 a first dielectric layer overlying the first reflector layer, and a second dielectric layer overlying the second reflector layer, the first and second dielectric layers composed of dielectric optical stacks including alternating high index and low index materials.

30 131. The pigment flake of claim 130, wherein the first and second dielectric layers have coating structures selected from the group consisting of  $(HL)^n$ ,  $(LH)^n$ ,  $(LHL)^n$ , and  $(HLH)^n$ , where  $n = 1-100$  and the L and H layers are 1 QW at a design wavelength.

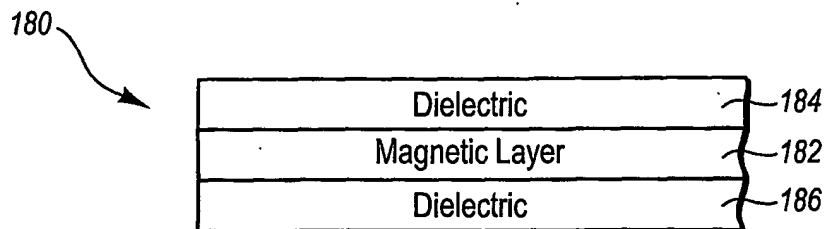
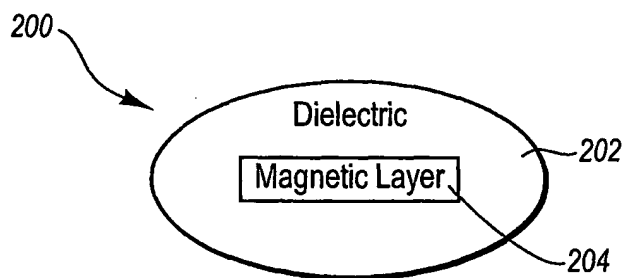
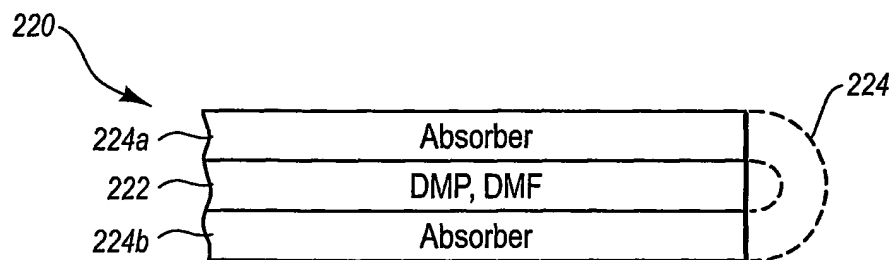
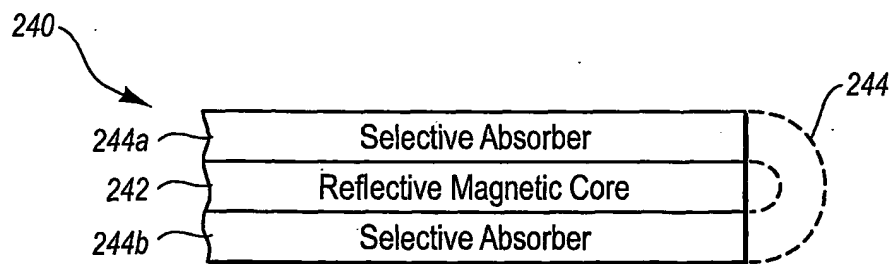
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**Fig. 1****Fig. 2****Fig. 3****Fig. 4**

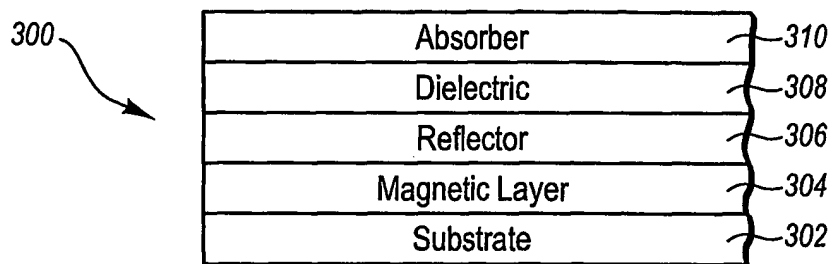
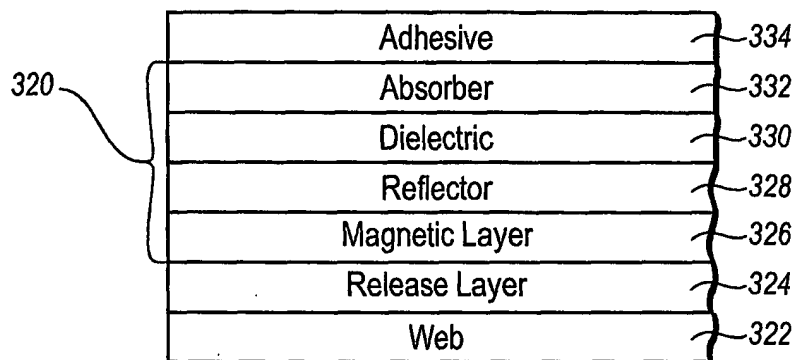
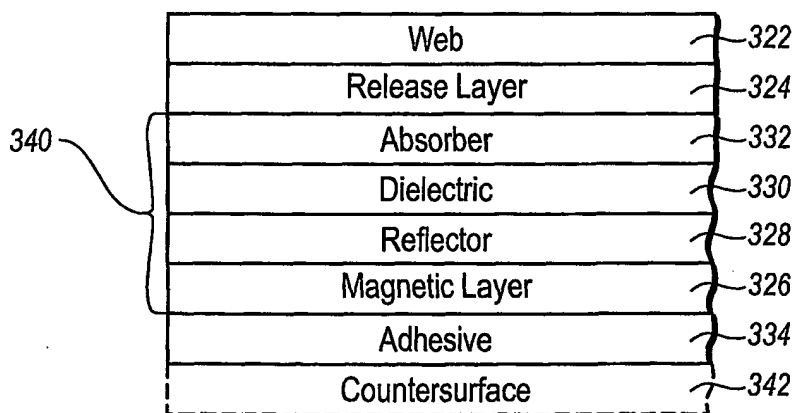
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**Fig. 5****Fig. 6****Fig. 7****Fig. 8**

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**Fig. 9****Fig. 10****Fig. 11****Fig. 12**

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**Fig. 13****Fig. 14****Fig. 15**

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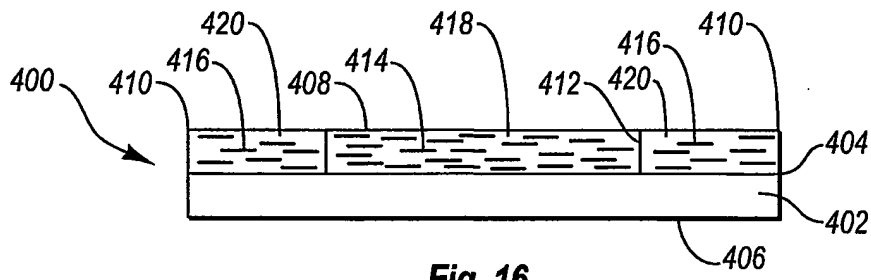


Fig. 16

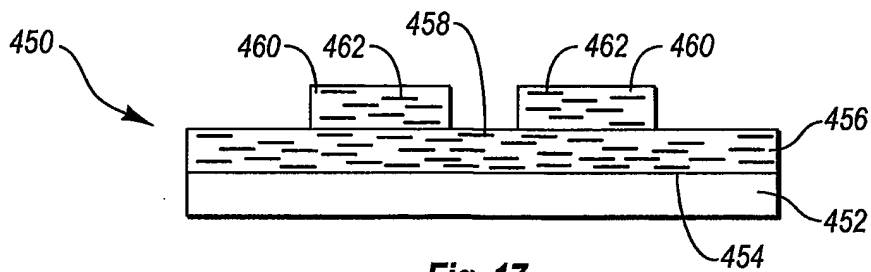


Fig. 17

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(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

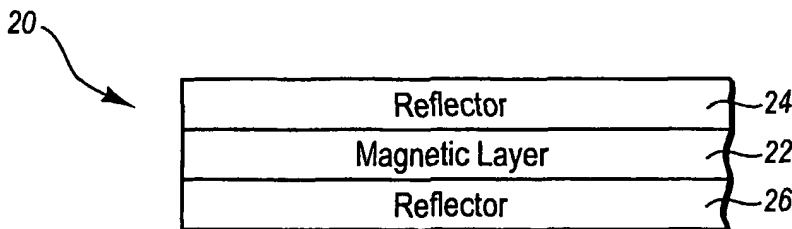
**Declarations under Rule 4.17:**

— as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG)

— as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT,

[Continued on next page]

(54) Title: MULTI-LAYERED MAGNETIC PIGMENTS AND FOILS



(57) Abstract: Multilayered magnetic pigment flakes and foils are provided. The pigment flakes can be a symmetrical coating structure on opposing sides of a magnetic core, or can be formed with the encapsulating coatings around the magnetic core. The magnetic core can be a magnetic layer between reflector or dielectric layers, a dielectric layer between magnetic layers, or only a magnetic layer. Some embodiments of the pigment flakes and foils exhibit a discrete color shift so as to have distinct colors at differing angles of incident light or viewing. The pigment flakes can be interspersed into liquid media such as paints or inks to produce colorant compositions for subsequent application to objects or papers. The foils can be laminated to various objects or can be formed on a carrier substrate.

WO 03/000801 A3



BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,  
NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM,  
GA, GN, GW, ML, MR, NE, SN, TD, TG)

(88) Date of publication of the international search report:  
27 February 2003

**Published:**

— with international search report

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 02/01059

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09C1/00 C09C1/24 H01F10/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09C G06K G08B H01F B42D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 341 002 A (FLEX PRODUCTS INC) 8 November 1989 (1989-11-08) column 1, line 3 - line 6 column 2, line 10 - line 58 column 3, line 6 - line 15; figures ---	1-22
X	DE 41 04 310 A (MERCK PATENT GMBH) 20 August 1992 (1992-08-20) column 1, line 42 - line 52 column 3, line 2 - line 10 column 3, line 34 - line 59 ---	1-22
E	EP 1 239 307 A (SICPA HOLDING SA) 11 September 2002 (2002-09-11) the whole document -----	1-22



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents :

\*A\* document defining the general state of the art which is not considered to be of particular relevance

\*E\* earlier document but published on or after the international filing date

\*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

\*O\* document referring to an oral disclosure, use, exhibition or other means

\*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*&\* document member of the same patent family

Date of the actual completion of the international search

26 November 2002

Date of mailing of the international search report

05/12/2002

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Authorized officer

Nobis, B

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 02/01059

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 23-131  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:  
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

## FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 23-131

In view of the large number and also the wording of the claims presently on file, which render it difficult, if not impossible, to determine the matter for which protection is sought, the present application fails to comply with the clarity and conciseness requirements of Article 6 PCT (see also Rule 6.1(a) PCT) to such an extent that a meaningful search is impossible. Consequently, the search has been carried out for those parts of the application which do appear to be clear (and concise), namely the subject-matter claimed in claims 1 to 22, a magnetic pigment flake comprising a central magnetic layer, and a first and a second reflector layer on the major surfaces thereof.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No  
PCT/US 02/01059

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			WO 02073250 A2	19-09-2002